

Handbook of Extractive Metallurgy

Edited by Fathi Habashi

Volume II: Primary Metals
Secondary Metals
Light Metals

 **WILEY-VCH**

Weinheim • Chichester • New York • Toronto • Brisbane • Singapore

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Cover Illustration: Michel Meyer/mmada

Library of Congress Card No. applied for
A CIP catalogue record for this book is available from the British Library

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Handbook of extractive metallurgy / ed. by Fathi Habashi. –
Weinheim ; New York ; Chichester ; Brisbane ; Singapore ; Toronto :
WILEY-VCH ISBN 3-527-28792-2

Vol. 1. The metal industry, ferrous metals. – 1997

Vol. 2. Primary metals, secondary metals, light metals. – 1997

Vol. 3. Precious metals, refractory metals, scattered metals, radioactive metals, rare earth metals. – 1997

Vol. 4. Ferroalloy metals, alkali metals, alkaline earth metals; Name index; Subject index. – 1997

© VCH Verlagsgesellschaft mbH – A Wiley company,
D-69451 Weinheim, Federal Republic of Germany, 1997

Printed on acid-free and low-chlorine paper

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Composition: Jean François Morin, Québec, Canada
Printing: Strauss Offsetdruck GmbH, D-69509 Mörlenbach
Bookbinding: Wilhelm Oswald & Co., D-67433 Neustadt/WeinstraÙe

Printed in the Federal Republic of Germany

Preface

Extractive metallurgy is that branch of metallurgy that deals with ores as raw material and metals as finished products. It is an ancient art that has been transformed into a modern science as a result of developments in chemistry and chemical engineering. The present volume is a collective work of a number of authors in which metals, their history, properties, extraction technology, and most important inorganic compounds and toxicology are systematically described.

Metals are neither arranged by alphabetical order as in an encyclopedia, nor according to the Periodic Table as in chemistry textbooks. The system used here is according to an economic classification which reflects mainly the uses, the occurrence, and the economic value of metals. First, the ferrous metals, i.e., the production of iron, steel, and ferroalloys are outlined. Then, nonferrous metals are subdivided into primary, secondary, light, precious, refractory, scattered, radioactive, rare earths, ferroalloy metals, the alkali, and the alkaline earth metals.

Although the general tendency today in teaching extractive metallurgy is based on the fundamental aspects rather than on a systematic description of metal extraction processes, it has been found by experience that the two approaches are complementary. The student must have a basic knowledge of metal extraction processes: hydro-, pyro-, and electrometallurgy, and at the same time he must have at his disposal a description of how a particular metal is extracted industrially from different raw materials and know what are its important compounds. It is for this reason, that this *Handbook* has been conceived.

The *Handbook* is the first of its type for extractive metallurgy. Chemical engineers have already had their Perry's *Chemical Engineers' Handbook* for over fifty years, and physical metallurgists have an impressive 18-volume *ASM Metals Handbook*. It is hoped that the

present four volumes will fill the gap for modern extractive metallurgy.

The *Handbook* is an updated collection of more than a hundred entries in *Ullmann's Encyclopedia of Industrial Chemistry* written by over 200 specialists. Some articles were written specifically for the *Handbook*. Some problems are certainly faced when preparing such a vast amount of material. The following may be mentioned:

- Although arsenic, antimony, bismuth, boron, germanium, silicon, selenium, and tellurium are metalloids because they have covalent and not metallic bonds, they are included here because most of them are produced in metallurgical plants, either in the elemental form or as ferroalloys.
- Each chapter contains the articles on the metal in question and its most important inorganic compounds. However, there are certain compounds that are conveniently described together and not under the metals in question for a variety of reasons. These are: the hydrides, carbides, nitrides, cyano compounds, peroxo compounds, nitrates, nitrites, silicates, fluorine compounds, bromides, iodides, sulfites, thiosulfates, dithionites, and phosphates. These are collected together in a special supplement entitled *Special Topics*, under preparation.
- Because of limitation of space, it was not possible to include the alloys of metals in the present work. Another supplement entitled *Alloys* is under preparation.
- Since the largest amount of coke is consumed in iron production as compared to other metals, the articles "Coal" and "Coal Pyrolysis" are included in the chapter dealing with iron.

I am grateful to the editors at VCH Verlagsgesellschaft for their excellent cooperation, in particular Mrs. Karin Sora who followed the project since its conception in 1994, and to

Jean-François Morin at Laval University for his expertise in word processing.

The present work should be useful as a reference work for the practising engineers and the students of metallurgy, chemistry, chemical engineering, geology, mining, and mineral beneficiation. Extractive metallurgy and the chemical industry are closely related; this *Handbook* will

therefore be useful to industrial chemists as well. It can also be useful to engineers and scientists from other disciplines, but it is an essential aid for the extractive metallurgist.

Fathi Habashi

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Primary Metals

																H	¹ H		
Li	Be													B	C	N	O	F	Ne
Na	Mg	Al													Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La [†]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac [‡]																	
†			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
‡			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

8 Copper

HARALD FABIAN † (§§ 8.1–8.10); HUGH WAYNE RICHARDSON (§ 8.11 EXCEPT 8.11.3.4); FATHI HABASHI (§ 8.11.3.4); ROBERT BESOLD (§ 8.12)

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8.1 Introduction

Copper, the red metal, apart from gold the only metallic element with a color different from a gray tone, has been known since the early days of the human race. It has always been one of the significant materials, and today it is the most frequently used heavy non-ferrous metal. The utility of pure copper is based on its physical and chemical properties, above all, its electrical and thermal conductivity (exceeded only by silver), its outstanding ductility and thus excellent workability, and its corrosion resistance (a chemical behavior making it a half-noble metal).

Its common alloys, particularly brass and bronze, are of great practical importance. Copper compounds ores are distinguished by bright coloration, especially reds, greens, and blues. Copper in soil is an essential trace element for most creatures, including humans.

Etymology. According to mythology, the goddess Venus (or Aphrodite) was born on the Mediterranean island of Cyprus, formerly Κύπρος (Greek), where copper was exploited millennia before Christ. Therefore, in early times the Romans named it cyprium, later called cuprum. This name is the origin of *copper* and of the corresponding words in most Romance and Germanic languages, e.g., *cobre* (Spanish and Portuguese), *cuiivre* (French), *Kupfer* (German), *koper* (Dutch), and *koppar* (Swedish).

A "cross with handle", from the Egyptian epoch, was called the mirror of Venus. In the alchemistic period, this sign meant the metal copper. Even now in astronomy it designates the planet Venus and in biology stands for "female".

History [21–24]. The first metals found by Neolithic man were gold and copper, later silver and meteoric iron. The earliest findings of copper are presumed to be nearly nine millennia old and came from the region near Konya in southern Anatolia (Turkey). Until recently the six-millennia-old copper implements from Iran (Tele Sialk) were presumed to be the

oldest. In the Old World, copper has been worked and used since approximately:

7000 B.C.	Anatolia
4000 B.C.	Egypt, Mesopotamia, Palestine, Iran, and Turkestan
3000 B.C.	Aegean, India
2600 B.C.	Cyprus
2500 B.C.	Iberia, Transcaucasia, and China
2200 B.C.	Central Europe
2000 B.C.	British Isles
1500 B.C.	Scandinavia

Empirical experience over millennia has led to an astonishing knowledge of copper metallurgical operations:

- Native copper was hardened by hammering (cold working) and softened by moderate heating (annealing).
- Heating to higher temperatures (charcoal and bellows) produced molten copper and made possible the founding into forms of stone, clay, and later metal.
- Similar treatment of the conspicuously colored oxidized copper ores formed copper metal.
- The treatment of sulfide copper ores (chalcocopyrite), however, did not result in copper metal, but in copper matte (a sulfidic intermediate). Not before 2000 B.C. did people succeed in converting the matte into copper by repeated roasting and smelting.
- In early times, bronze (copper–tin alloy) was won from complex ores, the Bronze Age beginning ca. 2800 B.C. At first, copper ores were smelted with tin ores; later, bronze was produced from metallic copper and tin. Brass (copper–zinc alloy) was known ca. 1000 B.C. and became widely used in the era of the Roman Empire.

In Roman times, most copper ore was mined in Spain (Rio Tinto) and Cyprus. With the fall of the Roman Empire, mining in Europe came to a virtual halt. In Germany (Saxony), mining activities were not resumed until 920 A.D. During the Middle Ages, mining and winning of metals expanded from Germany over the rest of Europe. In the middle of the 16th century, the current knowledge of metals was compiled in a detailed publication [23] by Georgius Agricola, *De Re Metallica* (1556).

Independent of the Old World, the Indians of North America had formed utensils by working native copper long before the time of Christ, although the skills of smelting and casting were unknown to them. On the other hand, the skill of copper casting was known in Peru ca. 500 A.D., and in the 15th century the Incas knew how to win the metal from sulfide ores.

Around 1500, Germany was the world leader in copper production, and the Fugger family dominated world copper trade. By 1800, England had gained first place, processing ores from her own sources and foreign pits into metal. Near 1850, Chile became the most important producer of copper ores, and toward the end of the last century, the United States had taken the world lead in mining copper ores and in production of refined copper.

Technical development in the copper industry has made enormous progress in the last 120 years. The blast furnace, based on the oldest principle of copper production, was continually developed into more efficient units. Nevertheless, after World War I, it was increasingly replaced by the reverberatory furnace, first constructed in the United States. Since the end of World War II, this furnace has been superseded slowly by the flash smelting furnace invented in Finland. Recently, several even more modern methods, especially from Canada and Japan, have begun to compete with the older processes.

An important development in producing crude metal was the application of the Bessemer converter concept to copper metallurgy by Manhès and David (France, 1880): this principle is still the most widely used method for copper converting in the world.

Over time the requirements for copper purity have become increasingly stringent. The invention and development of electrolysis by J. B. Elkington (England, 1865) and E. Wohlwill (Germany, 1876) made refining of high-purity copper possible.

In addition, the quantity of copper produced has increased immensely (Table 8.1). Since 1880, ca. 275×10^6 t was mined between 1800 and 1900.

Table 8.1: World mine production of copper (approximate, from several sources).

Year	Production, 10^3 t	Year	Production, 10^3 t
1700	9	1960	4200
1800	17	1965	5000
1850	57	1970	6400
1900	450	1975	7300
1950	2500	1980	7900
1955	3100	1984	8100

8.2 Physical Properties

Most properties of metallic copper depend on the degree of purity and on the source of the metal. Variations in properties are caused by:

- Grade of copper, i.e., the oxygen content: tough-pitch, deoxidized copper, oxygen-free copper
- Content of native impurities (e.g., arsenic) or remnants of additives (e.g., phosphorus), which form solid solutions or separate phases at the grain boundaries
- Thermal and mechanical pretreatment of the metal, which lead to states such as cast copper, hot-rolled copper, cold-worked (hard) copper, annealed (soft) copper, and sintered copper

These property differences are caused by the defects in the crystal lattice. Two groups of properties are to be distinguished:

- Low dependence on crystal lattice defects, e.g., caloric and thermodynamic properties, magnetic behavior, and nuclear characteristics
- High dependence on defects, e.g., electrical and thermal conductivity, plastic behavior, kinetic phenomena, and resistance to corrosion

The variations in properties are caused either by physical lattice imperfections (dislocations, lattice voids, and interstitial atoms) or by chemical imperfections (substitutional solid solutions).

Atomic and Nuclear Properties. The atomic number of copper is 29, and the atomic mass A , is 63.546 ± 0.003 (IUPAC, 1983). Copper consists of two natural isotopes, ^{63}Cu (68.94%) and ^{65}Cu (31.06%). There are also

nine synthetic radioactive isotopes with atomic masses between 59 and 68, of which ^{67}Cu has the longest half-life, ca. 58.5 h.

Crystal Structure. At moderate pressures, copper crystallizes from low temperatures up to its melting point in a cubic-closest-packed (ccp) lattice, type A1 (also F^1 or Cu) with the coordination number 12. X-ray structure analysis yields the following dimensions (at 20 °C):

Lattice constant	0.36152 nm
Minimum interatomic distance	0.2551 nm
Atomic radius	0.1276 nm
Atomic volume	7.114 cm ³ /mol

Density. The theoretical density at 20 °C, computed from lattice constant and atomic mass is 8.93 g/cm³. The international standard was fixed at 8.89 g/cm³ in 1913 by the IEC (International Electrotechnical Commission). The maximum value for 99.999% copper reaches nearly 8.96 g/cm³.

The density of commercial copper depends on its composition, especially the oxygen content, its mechanical and thermal pretreatment, and the temperature. At 20 °C, a wide range of values are found:

Cold-worked and annealed copper	8.89–8.93 g/cm ³
Cast tough-pitch electrolytic copper	8.30–8.70 g/cm ³
Cast oxygen-free electrolytic copper	8.85–8.93 g/cm ³

The values for cold-worked copper are higher than those of castings because the castings have pores and gas cavities.

The density of copper is nearly a linear function of temperature, with a discontinuity at the melting point:

t , °C	ρ , g/cm ³
solid copper: 20	8.93
600	8.68
900	8.47
1083	8.32
liquid copper: 1083	7.99
1200	7.81

The solidification shrinkage is 4%; the specific volume at 20 °C is 0.112 cm³/g.

Mechanical Properties. Important mechanical values are given in Table 8.2. High-purity copper is an extremely ductile metal. Cold working increases the hardness and tensile strength (hard or hard-worked copper); subse-

quent annealing eliminates the hardening and strengthening so that the original soft state can be reproduced (soft copper). The working processes are based on this behavior. Impurities that form solid solutions of the substitutional type likewise increase hardness and tensile strength.

Table 8.2: Mechanical properties of copper at room temperature.

Property	Unit	Annealed (soft) copper	Cold-worked (hard) copper
Elastic modulus	GPa	100–120	120–130
Shearing modulus	GPa	40–45	45–50
Poisson's ratio		0.35	
Tensile strength	MPa	200–250	300–360
Yield strength	MPa	40–120	250–320
Elongation	%	30–40	3–5
Brinell hardness (HB)		40–50	80–110
Vickers hardness (HV)		45–55	90–120
Scratch hardness		≈ 3	

Pure copper has outstanding hot workability without hot brittleness, but the high-temperature strength is low. Detrimental impurities, those that decrease the strength at high temperatures, are principally lead, bismuth, antimony, selenium, tellurium, and sulfur. The concentration of oxides of such elements at the grain boundaries during heating causes the embrittlement. However, such an effect can be desirable when free cutting is required. At subzero temperatures, copper is a high-strength material without cold brittleness.

The changes in typical mechanical properties such as tensile strength, elongation, and hardness by heat treatment result from recrystallization [25]. The dependence of recrystallization temperature and grain size on the duration of heating the amount of previous cold deformation and the degree of purity of copper can be determined from diagrams. The recrystallization temperature is ca. 140 °C for high-purity copper and is 200–300 °C for common types of copper. A low recrystallization temperature is usually advantageous, but higher values are required to maintain strength and hardness if the metal is heated during use.

Thermal Properties. Important thermal values are compiled in Table 8.3. The thermal

conductivity of copper is the highest of all metals except silver.

Table 8.3: Thermal properties of copper.

Property	Unit	Value
Melting point	K	1356 (1083 °C)
Boiling point	K	2868 (2595 °C)
Heat of fusion	J/g	210
Heat of vaporization	J/g	4810
Vapor pressure (at mp)	Pa	0.073
Specific heat capacity at 293 K (20 °C) and 100 kPa (1 bar)	J g ⁻¹ K ⁻¹	0.385
at 1230 K (957 °C) and 100 kPa		0.494
Average specific heat 273–573 K (0–300 °C) at 100 kPa (1 bar)	J g ⁻¹ K ⁻¹	0.411
273–1273 K (0–1000 °C) at 100 kPa		0.437
Coefficient of linear thermal expansion 273–373 K (0–100 °C)	K ⁻¹	16.9 × 10 ⁻⁶
273–673 K (0–400 °C)		17.9 × 10 ⁻⁶
between 273 and 1173 K (0–900 °C)		19.8 × 10 ⁻⁶
Thermal conductivity at 293 K (20 °C)	W m ⁻¹ K ⁻¹	394

Electrical properties. In practice, the most important property of copper is its high electrical conductivity; among all metals only silver is a better conductor. Both electrical conductivity and thermal conductivity are connected with the Wiedemann–Franz relation and show strong dependence on temperature (Table 8.4). The old American standard, 100% IACS (International Annealed Copper Standard), corresponds to 58.0 MS/m at 20 °C, and it is still widely used in the United States. The corresponding electrical resistivity (ρ) is $1.7241 \times 10^{-8} \Omega \cdot \text{cm}$, and the less usual resistivity based on weight (density of 8.89 g/cm³, IEC) is $0.1533 \text{ W} \cdot \text{g} \cdot \text{m}^{-1}$. The corresponding temperature coefficients are $0.0068 \times 10^{-8} \Omega \text{mK}^{-1}$ (dp/dT) and 0.00393 K^{-1} ($\rho^{-1} \text{dp}/\text{dT}$). The theoretical conductivity at 20 °C is nearly 60.0 MS/m or 103.4% IACS, and today commercial oxygen-free copper (e.g. C10200 or Cu–OF) has a conductivity of 101% IACS.

The factors that increase the strength decrease electrical conductivity: cold working and elements that form solid solutions. Ele-

ments that form oxidic compounds that separate at grain boundaries affect electrical properties only slightly. Copper may lose up to ca. 3% of its conductivity by cold working; however, subsequent annealing restores the original value. There is a simple rule: the harder the copper, the lower is its conductivity.

Other Properties. High-purity copper is diamagnetic with a mass susceptibility of $-0.085 \times 10^{-6} \text{ cm}^3/\text{g}$ at room temperature. The dependence on temperature is small. However, a very low content of iron can strongly affect the magnetic properties of copper.

The lower the frequency of light, the higher the reflectivity of copper. The color of a clean, solid surface of high-purity copper is typically salmon red.

The surface tension of molten copper is $11.25 \times 10^{-3} \text{ N/cm}$ at 1150 °C, and the dynamic viscosity is $3.5 \times 10^{-3} \text{ Pa} \cdot \text{s}$ at 1100 °C. Detailed physical-property information and data are to be found in the literature, particularly as tabular compilations [25–30].

Table 8.4: Temperature dependence of thermal and electrical conductivity of copper.

Temperature		Thermal conductivity, W m ⁻¹ K ⁻¹	Electrical conductivity, MS/m
K	°C		
17	-256	5000	
73	-200	574	460
113	-160	450	
173	-100	435	110
273	0	398	60
293	20	394	58
373	100	385	44
473	200	381	34
573	300	377	27
973	700	338	15

8.3 Chemical Properties

In the periodic table, copper is placed in period 4 and subgroup IB (together with silver and gold); therefore, it behaves as a typical transition metal. It appears in oxidation states +1 to +4, its compounds are colored, and it tends to form complex ions.

At relatively low temperature, copper(II) is the most stable state, but above 800 °C, copper(I) predominates, which is significant for pyrometallurgical processes; oxidation states

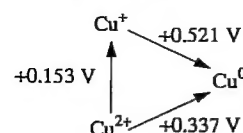
+3 and +4 were discovered in recent years in some coordination compounds.

The distribution of the 29 electrons is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. From this electron configuration, $[\text{Ar}]3d^{10}4s^1$, is derived the copper(I) ion (Cu^+) with a complete M shell (18 electrons). The copper(II) ion (Cu^{2+}) originates from the configuration $[\text{Ar}]3d^9 4s^2$, which has a slightly higher energy level.

The valence states and their radii determine the space lattice of alloys and compounds:

Species	Coordination number	Radius, nm
Cu^0	12	0.128
Cu^+	6	0.096
Cu^{2+}	6	0.072

The standard electrode potentials (at 25 °C) of copper correspond to the relative stabilities of the three species:



These values [31], or thermochemical data [32], in comparison with those of other elements, establish copper as a relatively noble metal.

Behavior in Air. Copper in dry air at room temperature slowly develops a thin protective film of copper(I) oxide. On heating to a high temperature in the presence of oxygen, copper forms first copper(I) oxide, then copper(II) oxide, both of which cover the metal as a loose scale.

In the atmosphere, the surface of copper oxidizes in the course of years to a mixture of green basic salts, the patina, which consists chiefly of the basic sulfate, with some basic carbonate. (In a marine atmosphere, there is also some basic chloride.) Such covering layers protect the metal.

Behavior versus Diverse Substances. While many substances scarcely react with copper under dry conditions, the rate of attack increases considerably in the presence of moisture. Copper has a high affinity for free halogens, molten sulfur, or hydrogen sulfide.

Therefore, copper is essentially not attacked by nonoxidizing acids, such as dilute sulfuric, hydrochloric, phosphoric, or acetic and other organic acids.

Dissolution of copper is possible either by oxidation or by formation of complexed copper ions. Thus, copper is soluble in oxidizing acids, such as nitric acid, hot concentrated sulfuric acid, and chromic acid, or in nonoxidizing acids containing an oxidizing agent such as oxygen or hydrogen peroxide. For example, acetic acid attacks copper in the presence of atmospheric oxygen to form verdigris, a green or greenish-blue pigment. In hydrometallurgical practice, metal compounds such as iron(III) sulfate, iron(III) chloride, and copper(II) chloride are suitable oxidizing agents.

The other method of dissolving copper is through formation of complex ions. The best reagents for this purpose are aqueous solutions of ammonia and ammonium salts or alkali-metal cyanides. However copper is essentially not attacked by alkali-metal hydroxide solutions.

Fresh water has practically no corrosive effect on copper, and seawater has only a small effect but wastewater containing organic sulfur-bearing compounds can be corrosive.

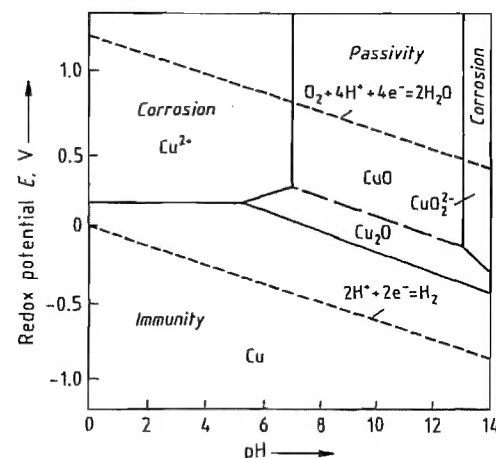


Figure 8.1: Pourbaix diagram for copper in highly dilute aqueous solution at normal temperature [35].

Corrosion [33–34]. M. J. N. Pourbaix has developed potential pH equilibrium diagrams for metals in dilute aqueous solutions [35]. Such

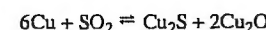
graphs give a rough indication of the feasibility of electrochemical reactions. Figure 8.1 shows the behavior of copper at room temperature and atmospheric pressure. The $\text{Cu-H}_2\text{O}$ system contains three fields of different character:

- Corrosion, in which the metal is attacked
- Immunity, in which reaction is thermodynamically impossible
- Passivity, in which there is no cause of kinetic phenomena

Gases and Copper [36–37]. An exact knowledge of the behavior of solid and liquid copper toward gases is important for production and use of the metal. With the exception of hydrogen, the solubility of gases in molten copper follows Henry's law: the solubility is proportional to the partial pressure.

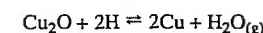
Oxygen dissolves in molten copper as copper(I) oxide up to a concentration of 12.65 % Cu_2O (corresponding to 1.4 % O) (also see Figure 8.22). Copper(I) oxide in solid copper forms a separate solid phase.

Sulfur dioxide dissolves in molten copper and reacts:



Hydrogen is considerably soluble in liquid copper, and after solidification some remains dissolved in the solid metal, although copper does not form a hydride. The solubility follows Sievert's law, being proportional to the square root of the partial pressure because the H_2 molecules dissociate into H atoms on dissolution. Hydrogen has high diffusibility because of its extremely small atomic volume.

Hydrogen dissolved in oxygen-bearing copper reacts with copper(I) oxide at high temperatures to form steam:



Steam is not soluble in copper; therefore, it either escapes or forms micropores.

Nitrogen, carbon monoxide, and carbon dioxide are practically insoluble in liquid or solid copper. Hydrocarbons generally do not react with copper. An exception, acetylene (ethyne), reacts at room temperature to form the highly explosive copper acetylides Cu_2C_2 and CuC_2 ; therefore, acetylene gas cylinders must not be equipped with copper fittings.

Table 8.5: Typical copper contents of natural materials.

Mineral	Content, ppm
Basalt	85
Diorite	30
Granite	10
Sandstone	1
Copper ores (poor)	5 000
Copper ores (rich)	50 000
Native copper	950 000
Seawater	0.003
Deep-sea clays	200
Manganese nodules	10 000
Marine ore sludges	10 000
Earth's crust (average)	50
Meteorites (average)	180

8.4 Occurrence

In the upper part of the earth's crust (16 km deep), the average copper content is ca. 50 ppm. Older estimates were nearly 100 ppm, while recent spectral analysis values are 30–40 ppm. Copper is 26th in order of abundance of the elements in the accessible sphere of the earth. Table 8.5 shows average copper contents in natural materials.

8.4.1 Copper Minerals

More than 200 minerals contain copper in definable amounts, but only ca. 20 are of importance as copper ores (Table 8.6) or as semiprecious stones (turquoise and malachite). Copper is a typical chalcophilic element; therefore, its principal minerals are sulfides, mostly chalcopyrite, bornite, and chalcocite, often accompanied by pyrite, galena, or sphalerite.

Table 8.6: The most important copper minerals.

Mineral	Formula	Copper	Crystal system	Density, g/cm ³
Native copper	Cu	≤ 99.92	cubic	8.9
Chalcocite	Cu ₂ S	79.9	orthorhombic	5.5–5.8
Digenite	Cu ₉ S ₅	78.0	cubic	5.6
Covellite	CuS	66.5	hexagonal	4.7
Chalcopyrite	CuFeS ₂	34.6	tetragonal	4.1–4.3
Bornite	Cu ₅ FeS ₄ /Cu ₃ FeS ₃	55.5–69.7	tetragonal	4.9–5.3
Tennantite	Cu ₁₂ As ₄ S ₁₃	42–52	cubic	4.4–4.8
Tetraedrite	Cu ₁₂ Sb ₄ S ₁₃	30–45	cubic	4.6–5.1
Enargite	Cu ₃ As ₄ S ₄	48.4	orthorhombic	4.4–4.5
Bournonite	CuPbSbS ₃	13.0	orthorhombic	5.7–5.9
Cuprite	Cu ₂ O	88.8	cubic	6.15
Tenorite	CuO	79.9	monoclinic	6.4
Malachite	CuCO ₃ ·Cu(OH) ₂	57.5	monoclinic	4.0
Azurite	2CuCO ₃ ·Cu(OH) ₂	55.3	monoclinic	3.8
Chrysocolla	CuSiO ₃ ·nH ₂ O	30–36	(amorphous)	1.9–2.3
Diopside	Cu ₆ [Si ₆ O ₁₈]·6H ₂ O	40.3	rhombohedral	3.3
Brochantite	CuSO ₄ ·3Cu(OH) ₂	56.2	monoclinic	4.0
Antlerite	CuSO ₄ ·2Cu(OH) ₂	53.8	orthorhombic	3.9
Chalcanthite	CuSO ₄ ·5H ₂ O	25.5	triclinic	2.2–2.3
Atacamite	CuCl ₂ ·3Cu(OH) ₂	59.5	orthorhombic	3.75

Secondary minerals are formed in sulfide ore bodies near the earth's surface in two stages. In the oxidation zone, oxygen-containing water forms copper oxides, subsalts (subcarbonates and subsulfates), and silicates. In the deeper cementation zone, copper-bearing solutions from these salts are transformed into secondary copper sulfides (chalcocite and covellite) and even native copper of often high purity, e.g., in the Michigan copper district (Keweenaw Peninsula).

Other metallic elements frequently found in copper ores are iron, lead, zinc, antimony, and arsenic; less common are selenium, tellurium, bismuth, silver, and gold. Substantial enrichments sometimes occur in complex ores. For example, ores from Sudbury, Ontario, in Canada contain nickel and copper in nearly the same concentrations, as well as considerable amounts of platinum metals. The copper ores from Zaire and Zambia are useful sources of cobalt. Many porphyry copper ores in America contain significant amounts of molybdenum and are the most important single source of rhenium. The extraction of precious metals and other rare elements can be decisive for the profitability of copper mines, smelters, and refineries.

8.4.2 Origin of Copper Ores

Ore deposits are classified according to their mode of formation, but the origin of copper ores is geologically difficult to unravel, and some of the proposed origins are controversial. The classification distinguishes two main groups, the magmatic series and the sedimentary series.

Magmatic Ore Formation. This involves magma crystallization and comprises the following groups:

- Liquid magmatic ore deposits originate by segregation of the molten mass so that the heavier sulfides (corresponding to matte) separate from the silicates (corresponding to slag) and form intrusive ore bodies. Examples: Sudbury, Ontario; Norilsk, western Siberia.
- Pegmatitic-pneumatolytic ore deposits develop during the cooling of magma to ca. 374 °C, the critical temperature of water. Examples: Bisbee, Arizona; Cananea, Mexico.
- Hydrothermal ore deposits result by further cooling of the hot, dilute metal-bearing solutions from ca. 350 °C downward, i.e., below the critical temperature of water. Such deposits contain copper primarily as chalcocopyrite and satisfy ca. 50 % of the demand

in the Western world. There are many examples of different types of hydrothermal deposits. Examples: Butte, Montana (gangue deposit); Tsumeb, Namibia (metasomatic deposit); Bingham Canyon, Utah; Chuquibambilla, Chile; Toquepala, Peru; Bougainville, Solomon Islands (impregnation deposits). Impregnation deposits are also called disseminated copper ores or porphyry copper ores (or simply porphyries) because of their fine particle size.

- Exhalative sedimentary ore deposits originate from submarine volcanic exhalations and thermal springs that enter into seawater, and constitute a transitional type to sedimentary deposits. These ores are third in economic importance in the Western world. The actual formation of such sulfidic precipitations can be observed, for example, the marine ore slimes in the Red Sea. Examples: Mount Isa, Queensland; Rio Tinto, Spain; Kammelsberg (Harz), Germany.

Sedimentary Ore Formation. The origin of sedimentary ore occurs in the exogenous cycle of rocks and may be subdivided into the following groups:

- Arid sediment in sandstones and conglomerates occur widely in Russia as widespread continental zones of weathering with uneven mineralization. Examples: Dsheskasgan, Kazakhstan; Exótica, Chile.
- Partly metamorphized sedimentary ores in shales, marls, and dolomites form large strata-bound ore deposits, especially in the African copper belt, and represent the second most important source of copper to the Western world, as well as supplying nearly 75 % of its cobalt. Examples: Zaire (oxidation zone, oxidized ores ≤ 6 % Cu); Zambia (cementation zone, secondary sulfide ores, ≤ 4 % Cu).
- Marine precipitates have formed sedimentary ore deposits similar to the present phenomenon of sulfide precipitation by sulfur bacteria in the depths of the Black Sea. Examples: Mansfeld (copper schist), Germany; Silesia (copper marl), Poland.

- Deep-sea concretions lie in abundance on the bottom of the oceans, especially the Pacific Ocean. These so-called manganese nodules could also be a source of copper in the future.

8.4.3 Copper Ore Deposits

Geologically, the main regions of copper ore deposits are found in two formations: the Precambrian shields and the Tertiary fold mountains and archipelagos. There are major producing countries on every continent [38].

- North America: United States (Arizona, Utah, New Mexico, Montana, Nevada, and Michigan), Canada (Ontario, Quebec, British Columbia, and Manitoba), and Mexico (Sonora)
- South America: Chile, Peru, and Brazil
- Africa: Zaire, Zambia, Zimbabwe, South Africa, and Namibia
- Australia and Oceania: Queensland, Papua New Guinea
- Asia: Russia (Siberia, Kazakhstan, and Uzbekistan), Japan, Philippines, Indonesia, India, Iran, and Turkey
- Europe: Poland (Silesia), Yugoslavia, Spain (Huelva), Norway, Sweden, and Finland

Antarctica may be an important copper ores in the foreseeable future.

Table 8.7: Copper ore reserves in 1983 of the most important producing countries of the Western world [41–42].

Country	Ore reserves, × 10 ⁶ t	Percentage of world reserves
United States	99.6	21.1
Chile	96.5	20.5
Peru	30.6	6.5
Zambia	30.3	6.4
Zaire	29.6	6.3
Canada	27.4	5.8
Mexico	23.1	4.9
Australia	16.1	3.4
Panama	12.7	2.7
Philippines	11.9	2.5
Papua New Guinea	10.8	2.3
Brazil	10.0	2.1
Total	398.6	84.5

8.4.4 Copper Resources

The copper contents of the worldwide primary copper reserves are listed in Table 8.7. Reserves are the identified (measured, indicated, and inferred) resources and do not include undiscovered (hypothetical and speculative) resources. In the course of time, the available reserves increase in consequence of both technological progress in the processing of ores with low copper content or undesirable impurities and the discovery of new ore deposits [39–40]. In 1982 the world reserves were estimated at 505×10^6 t of copper. The total land-based resources were estimated at 1.6×10^9 t of copper. In addition there is an estimated 700×10^6 t of copper in deep-sea nodules.

If one assumes that total production will remain stable, the identified resources would last until ca. 2050, which is the static outlook. In contrast, the dynamic approach which assumes that production will increase at the rate it has in recent years, would reduce the duration of known reserves by nearly half. If one considers all copper resources, these times would be at least doubled. However, all of these forecasts are quite unreliable. In addition, the forecasts do not take into consideration secondary copper (recycling scrap).

8.4.5 Mining

Exploration, which is the search for ore deposits and their subsequent detailed investigation, is required to ascertain the commercial feasibility of a potential mine. Many geological, geochemical, and geobotanical methods are available, but all are complicated and expensive. Often legal and political factors are more decisive than technological aspects. The average copper content of ores is an essential factor. In 1900, this content worldwide was ca. 5% Cu. Today it is ca. 1%; nevertheless, this represents a ca. 200-fold enrichment of the average in the earth's crust. High-grade deposits (> 6% Cu) are largely exhausted.

For economic reasons, modern copper mining must have high capacity, which means ex-

tensive mechanization. The high cost of mining and of ore beneficiation contributes up to two-thirds of the final price of copper.

There are several methods of mining copper ores:

- Open-pit (surface) mining
- Underground (deep) mining
- In situ leaching (solution mining)
- Ocean mining

At present, the greatest part of primary copper comes from open-pit mines, mostly from porphyry ores. The first open-pit mine was started at Bingham Canyon, Utah, early in this century; other big mines are found in Chuquibambilla, Chile and Toquepala, Peru. Profitable open-pit production requires large ore bodies near the surface with a minimum copper content of 0.5% (in some cases, as low as 0.3%) in sulfidic form for subsequent beneficiating by froth flotation.

Underground mining has been practiced for millennia. However, in the last few decades the competition of open-pit mining has made such older underground methods as overhand and underhand stoping uneconomical. Newer procedures such as open stoping or block caving can be used if good ores occur in deep deposits. The copper concentration should exceed 1%, and some content of other profitable metals is desirable.

In situ leaching is a hydrometallurgical process in which copper is extracted by chemical dissolution in sulfuric acid. This method is suitable for low-grade copper ore bodies for which customary mining operations would be uneconomical as well as for the leaching of remnant ores from abandoned mines. In some cases, the ore body must be broken before leaching by blasting with explosives to increase the surface area for chemical reaction.

A recent development is ocean mining, which involves obtaining metalliferous raw materials from the deep oceanic zones. Two groups of substances are of interest: deep-sea nodules [43] and marine ore slimes [44]. The nodules (manganese nodules) contain, in addition to iron oxides, ca. 25% Mn, 1% Ni, 0.35% Co, and 0.5% (max. 1.4%) Cu. Spe-

cially equipped ships have collected and lifted these nodules from depths of 3000–5000 m; specific metallurgical and chemical methods for processing the nodules have been developed in pilot plants. Because of the extremely high expenses, large-scale operations of this type have not yet been undertaken. Marine ore slimes from the Red Sea (2200-m depth) average ca. 4% Zn, 1% Cu, and a little silver. Although methods for processing these slimes have been investigated, this resource is not now economically important.

8.5 Production

Over the years copper production methods have been subjected to a continual selection process because of the need [45] for (1) increased productivity through rationalization, (2) lower energy consumption, (3) increased environmental protection, (4) increased reliability of operation, and (5) improved safety in operation. During this development a number of tendencies have become apparent:

- Decrease in the number of process steps
- Preference for continuous processes over batch processes
- Autogenous operation
- Use of oxygen or oxygen-enriched air
- Tendency toward electrometallurgical methods
- Increased energy concentration per unit of volume and time
- Electronic automation, measurement, and control
- Recovery of sulfur for sale or disposal
- Recovery of valuable byproducts

The selection of a particular production method depends essentially on the type of available raw materials, which is usually ore or concentrate and on the conditions at the plant location.

About 80% of the primary copper in the world comes from low-grade or poor sulfide ores, which are usually treated by pyrometallurgical methods, generally in the following sequence:

- Beneficiation by froth flotation to get a concentrate
- Optional partial roasting to obtain oxidized material or calcines
- Two-stage pyrometallurgical treatment
 - a) smelting concentrates to matte
 - b) converting matte by oxidation to crude (converter or blister) copper
- Refining the crude copper, usually in two steps
 - a) pyrometallurgically to fire-refined copper
 - b) electrolytically to high-purity electrolytic copper

About 15% of the primary copper originates from low-grade oxidized (oxide) or mixed (oxidized and sulfidic) ores. Such materials are generally treated by hydrometallurgical methods.

The very few high-grade or rich copper ores still available can be processed by traditional smelting in a shaft furnace. This process is also used for recovering copper from secondary materials such as intermediate products scrap and wastes.

Figure 8.2 illustrates the most important operations in copper extraction from various copper ores.

8.5.1 Beneficiation

Most sulfide copper ores must be beneficiated to increase the metal content. The essential operation is froth flotation, which is usually carried out in two successive steps: the first is collective or bulk flotation for concentrating all the metal-containing minerals, and the second, if necessary, is selective flotation to separate the various minerals [47].

Figure 8.3 shows the reduction in total mass with simultaneous enrichment of copper content in the steps from ore to metal. Modern dressing plants are always built near the mines to reduce the transportation costs and are constructed in a relatively uniform manner. The first operation is the comminution of lumpy ores to a pulp in the following stages:

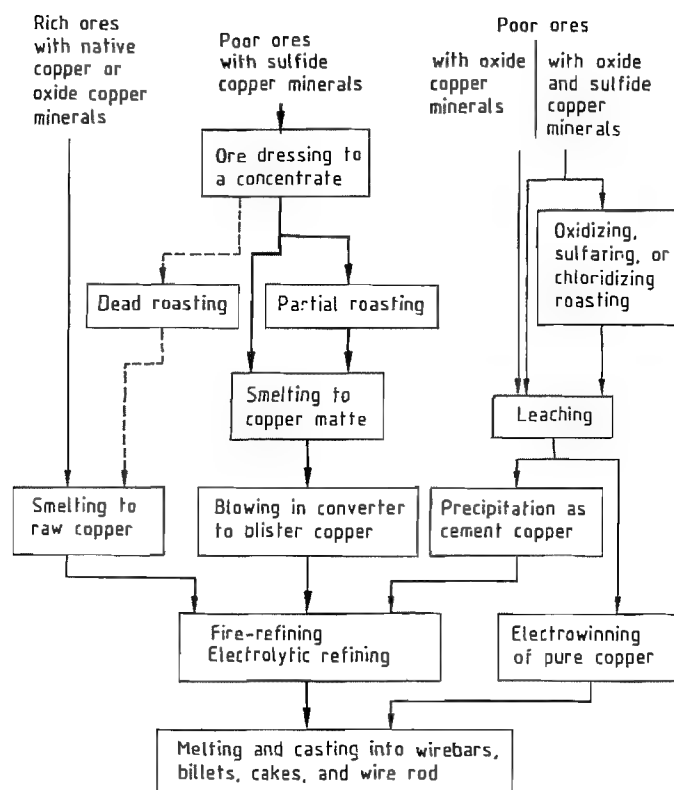


Figure 8.2: The most important stages in copper production [46].

- Crushing in jaw, gyratory, and cone crushers
- Sizing on vibrating screens
- Wet grinding in rod and ball mills or, more recently, by autogenous milling

Classifying in classifiers and hydrocyclones. The separation of the feed pulp into metal sulfides and gangue or into different sulfide groups is done by froth flotation using frothers, collectors, activators, depressers, and reagents to control the pH (e.g., lime). In simple cases, the flotation cells are combined into three groups with three distinct functions:

- Rougher flotation for sorting into preconcentrate and tailings
- Cleaner flotation for posttreatment of preconcentrate
- Scavenger flotation for posttreatment of the tailings from the first step

Figure 8.4 illustrates the relationship among these three operations, omitting the intermediate grinding steps.

The next step is solid-fluid separation by sedimentation in settlers and thickeners with subsequent vacuum filtering by drum and disk filters. The residual moisture is 8–12% and the concentrates are usually shipped in this condition. In a few cases, the pulp is conveyed in pipelines. Dewatered concentrates may heat spontaneously or even catch fire; therefore, appropriate precautions must be taken [48].

The copper content of dried chalcopyrite concentrates (CuFeS_2) averages 20–30%, rarely less, but considerably more if chalcosite (Cu_2S) is present. The average particle size is determined by the flotation conditions and is generally between 0.25 and 0.01 mm.

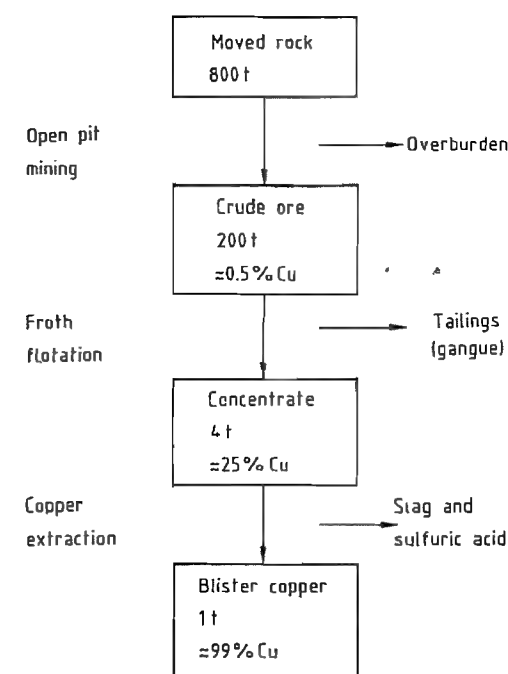


Figure 8.3: Enrichment of copper from ore to metal.

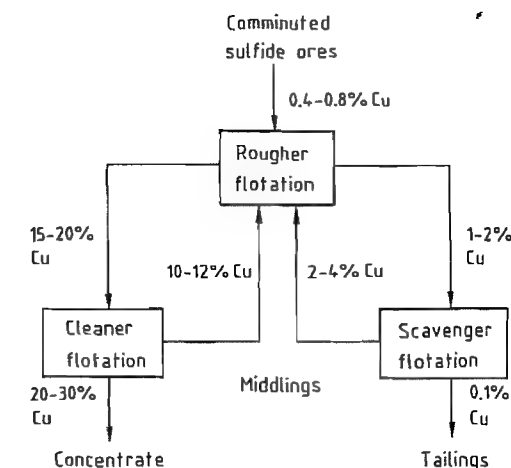


Figure 8.4: Froth flotation of sulfide copper ores.

8.5.2 Segregation

Special low-grade oxidized copper ores that are not economically usable by current methods, especially hydrometallurgical processes, occur in large ore bodies in Africa and

America. These contain copper mostly as silicates (chrysocolla and diopside), and because of their high content of silica and often limestone, they are treated by segregation, a process known for more than 60 years and recently used sporadically in the so-called TORCO (treatment of refractory copper ores) process. The chemical reactions are complicated: ore, gangue, and furnace gases react with added sodium chloride and pulverized coal or coke to form copper(I) chloride and then metallic copper, which is sulfidized and collected by flotation. TORCO [50] plants were built in Zambia and Mauretania, and a variant, the Mitsui segregation process, has been installed in Peru [51].

8.5.3 Roasting

Roasting may be used to prepare sulfide concentrates for subsequent pyrometallurgical or hydrometallurgical operation. For pyrometallurgical processing, the purpose of roasting is to decrease the sulfur content to an optimum level for smelting to copper matte. In many modern processes, however, roasting is not a separate step, but is combined with matte smelting. For hydrometallurgical extraction, roasting forms compounds that can be leached out.

The roasting process, which produces the so-called calcines, has several effects:

- Drying the concentrates
- Oxidizing a part of the iron present
- Controlling the sulfur content
- Partially removing volatile impurities, especially arsenic
- Preheating the calcined feed with added fluxes, chiefly silica and limestone

Chemical Reactions. When the moist concentrates, which contain many impurity elements are heated, a multitude of chemical reactions occur. Because analysis of the many thermodynamic equilibria is not practical, a few fundamental systems are usually chosen. The most important is the ternary copper–oxygen–sulfur system (Figure 8.5). The next most important system is the ternary iron–oxygen–

sulfur system because most sulfidic copper ores contain significant amounts of iron.

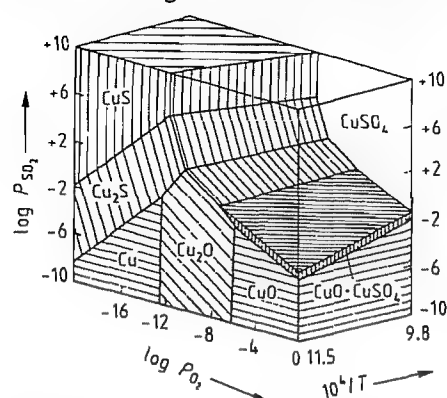
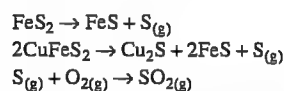
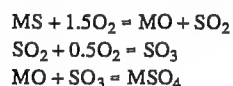


Figure 8.5: Partial phase diagram of the ternary Cu-O-S system [52].

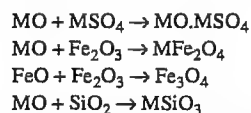
Initially, sulfides such as pyrite and chalcopyrite decompose and generate sulfur vapor, which reacts with oxygen to form sulfur dioxide:



The principal reactions, i.e., the formation of metal (= M) oxides, sulfur trioxide, and metal sulfates, are exothermic.



In addition, there are secondary reactions such as the formation of basic sulfates, ferrites (especially magnetite), and silicates, the last providing most of the slag in the subsequent smelting:



Methods. There are several important roasting methods; all involve oxidation at an elevated temperature, generally between 500 and 850 °C:

- **Partial (oxidizing) roasting** is the conventional way of extracting copper from sulfide concentrates. At 800–850 °C, the degree of roasting is determined by controlling the ac-

cess of air. A predetermined amount of sulfur is removed and only part of the iron sulfide is oxidized. The copper sulfide is relatively unchanged. These conditions are important for the formation of a suitable matte.

- **Total, or dead, roasting** is occasionally used for complete oxidation of all sulfides for a subsequent reduction process or for special hydrometallurgical operations.
 - **Sulfatizing roasting** is carried out at 550–565 °C to form sulfates. This method yields calcines well-suited for hydrometallurgical treatment.
 - **Chloridizing roasting** involves sulfatizing roasting with addition of sodium chloride. The temperature should not exceed 600 °C to avoid loss of copper(I) chloride. This treatment, which was developed by the Duisburger Kupferhütte, Germany, is limited to pyrite cinders for subsequent leaching and precipitating [53]; however, the process was discontinued several years ago.
 - **Chloridizing volatilization** involves heating to ca. 1200 °C in the presence of calcium chloride so that various metal chlorides and other volatile compounds can be separated. The Finnish Vuoksenniska process, which used this procedure, was discontinued years ago. Recently a Japanese company started up a similar procedure.
- The roasted product is obtained in one of three states, depending on the maximum roasting temperature:
- **Low temperature.** The roasted concentrates remain in the same state as before (solidus range).
 - **Intermediate temperature.** A sinter forms if some liquid phase appears (range of softening).
 - **High temperature.** The whole feed melts during roasting (liquidus range).
- Roasters.** Only a few roaster designs are now used.
- **Multiple-hearth furnaces**, which produce pulverous calcines, were the most widely used type (in various models, e.g., the well-known Herreshoff furnace) until the middle

of the 20th century. Since then, they have been increasingly displaced by the fluidized-bed roaster.

- **Fluidized-bed reactors**, the most modern type, also yield pulverous calcines. Their two key advantages are exploitation of waste heat and high productivity in consequence of favorable kinetic reaction conditions. The reactors are 5–12 m high and have a diameter of 4–8 m. Examples: Anaconda Co., Butte, Montana; RTB Bor, Bor, Yugoslavia.
 - **Sintering (blast) roasters** are used only if concentrates are to be processed in blast furnaces (see the *Blast Furnace Smelting* section). The most important type is the Dwight-Lloyd sinterer. Example: Lubumbashi smelter Zambia.
 - **Flash smelting furnaces** combine roasting and smelting in the same unit (see the *Autogenous Smelting* section).
- The average residence time of concentrate in the various roasters is very different:
- | | |
|-------------------------|---------------|
| multiple-hearth furnace | a few hours |
| sintering apparatus | a few minutes |
| fluidized-bed reactor | a few seconds |

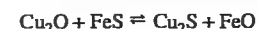
The roaster gases that are generated contain sulfur dioxide, which is generally converted to sulfuric acid in contact acid plants. The SO₂ content in the roast gas is ca.
5–8 vol % for multiple-hearth furnaces
8–15 vol % for fluidized-bed reactors

8.5.4 Pyrometallurgical Principles

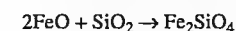
Smelting of unroasted or partially roasted sulfide ore concentrates produces two immiscible molten phases: a heavier sulfide phase containing most of the copper, the *matte*, and an oxide phase, the *slag*. In most copper extraction processes matte is an intermediate.

8.5.4.1 Behavior of the Components

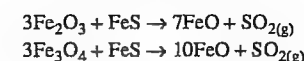
The most important equilibrium matte smelting is that between the oxides and sulfides of copper and iron:



Iron(II) oxide reacts with added silica flux to form fayalite, a ferrous silicate that is the main component of slag:



Liquid iron sulfide reduces higher iron oxides to iron(II) oxide:



The second reaction serves to remove magnetite, which complicates furnace operations because of its high melting point (1590 °C) [55].

The pyrometallurgical production of copper from sulfide ore concentrates may be considered as a rough separation of the three main elements as crude copper, iron(II) silicate slag, and sulfur dioxide. About 20 accompanying elements must be removed from the copper by subsequent refining. Table 8.8 shows the distribution of important impurities among matte slag and flue dust. Precious metals, such as silver gold, platinum, and palladium, collect almost entirely in the matte, whereas calcium, magnesium, and aluminum go into the slag.

Table 8.8: Average percentage distribution of the accompanying elements in copper smelting [20].

Element	Matte	Slag	Flue dust
Arsenic	35	55	10
Antimony	30	55	15
Bismuth	10	10	80
Selenium	40	—	60
Tellurium	40	—	60
Nickel	98	2	—
Cobalt	95	5	—
Lead	30	10	60
Zinc	40	50	10
Tin	10	50	40
Silver and gold	99	1	—

8.5.4.2 Matte

The ternary Cu-Fe-S system is discussed in detail in the literature [56–58]. Figure 8.6 shows the composition of the pyrometallurgically important copper mattes and the liquid-phase immiscibility gap between matte and the metallic phase. In the liquid state, copper matte is essentially a homogeneous mixture of copper(I) and iron(II) sulfides: the pseudobinary Cu₂S–FeS system.

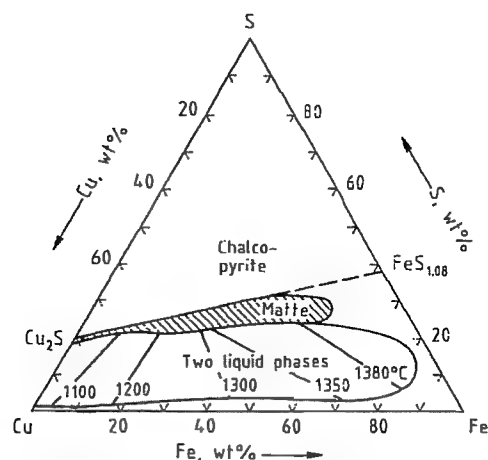


Figure 8.6: Ternary Cu-Fe-S diagram showing copper mattes and the miscibility gap [56].

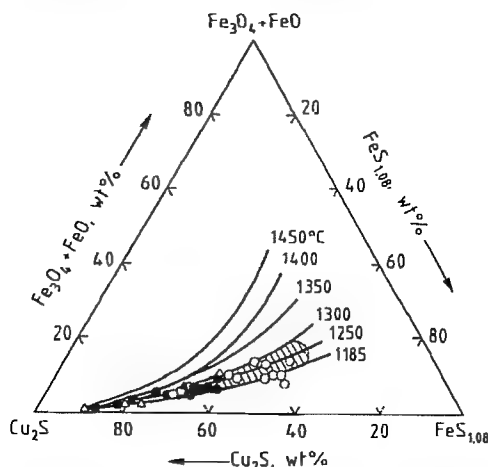


Figure 8.7: Partial ternary $\text{Cu}_2\text{S}-\text{FeS}_{1.08}-(\text{Fe}_3\text{O}_4 + \text{FeO})$ diagram [59] showing mattes from various processes. O Reverberatory furnace; Δ Flash smelting furnace; ▲ Electric furnace; ● Blast furnace; ■ Converter.

Arsenides and antimonides are soluble in molten matte, but their solubility decreases with an increasing percentage of copper in the matte. Accordingly, when the arsenic concentration is high, a special phase, the so-called *speiss*, can separate. It is produced under reducing conditions in the blast furnace, and its decomposition is complicated.

Compositions of several copper mattes are shown in the partial diagram $\text{Cu}_2\text{S}-\text{FeS}-(\text{Fe}_3\text{O}_4 + \text{FeO})$ (Figure 8.7), which is a section

of the quaternary Cu-Fe-O-S system. The density of solid copper mattes ranges between 4.8 g/cm^3 (FeS) and 5.8 g/cm^3 (Cu_2S); liquid mattes have the following densities: 4.1 g/cm^3 (30% Cu, 40% Fe, 30% S), 4.6 g/cm^3 (50% Cu, 24% Fe, 26% S), and 5.2 g/cm^3 (80% Cu, 20% S).

8.5.4.3 Slags

Slags from copper matte smelting contain 30–40% iron in the form of oxides and about the same percentage of silica (SiO_2), mostly as iron(II) silicate. Such slags can be considered as complex oxides in the $\text{CaO}-\text{FeO}-\text{SiO}_2$ system [60] or, because of the relatively low CaO content of most slags, in the partial diagram $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ [61] (Figure 8.8). Ternary systems of these and other pertinent oxide systems are found in the literature [62–63]. Table 8.9 shows the general composition of some slag types. Important properties of copper slag systems are compiled in [64].

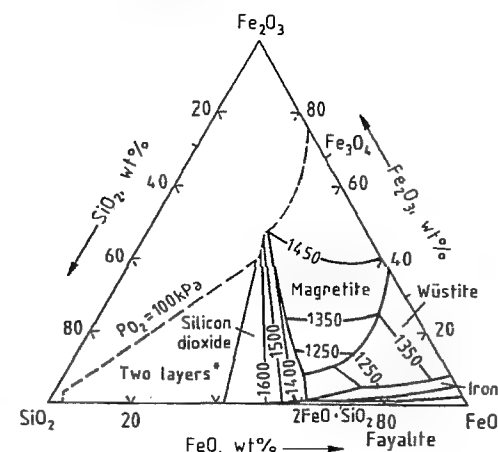


Figure 8.8: Ternary $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ diagram [61].

The objectives of matte smelting are to achieve a rapid complete separation of matte and slag, the two immiscible phases, and a minimal copper content in the slag. The differing properties of slag and matte affect this separation:

- the low, narrow melting interval of slag

- the low density of liquid slag (ca. $3.1\text{--}3.6 \text{ g/cm}^3$) and the difference in density between molten matte and slag of ca. 1 g/cm^3

- the low viscosity and high surface tension of the slag

The ratio of the weight percent of copper in matte to that of copper in slag should be between 50 and 100. High matte grades generally cause high copper losses in 'slag'. Such losses depend on the mass ratio of slag to copper produced, which is usually between 2 and 3. Copper in slags occurs in various forms, including suspended matte, dissolved copper(I) sulfide, and slagged copper(I) oxide, partially as a silicate, which is typical of nonequilibrium processing.

Slags containing < 0.8% copper are either discarded as waste or sold as products with properties similar to those of natural basalt (crystalline) or obsidian (amorphous). When liquid slag is cooled slowly, it forms a dense, hard crystalline product that can be used as a large-size fill for riverbank protection or dike construction and as a medium-size crushed fill for roadbeds or railway ballast. Quick solidification, by pouring molten slag into water, gives amorphous granulated slag, an excellent abrasive that has partially supplanted quartz sand. Ground granulated slag is used as a trace element fertilizer because of its copper and other nonferrous metals.

Most of the newer copper smelting processes produce high-grade mattes, and the short residence time of the materials in the reaction chamber results in an incomplete approach to chemical equilibrium. Both factors lead to high amounts of copper in the slag, generally > 1%. Such slags must be treated by special methods for copper recovery.

Table 8.9: Composition (%) of typical copper smelter slags [65].

Component	Reverberatory furnace	Flash furnace	Noranda reactor	Peirce-Smith converter
Copper	0.4–0.6	1–1.5	8–10	3–5
Iron (total)	35	40	35	50
Silica	38	30	21	25
Magnetite	7–12	13	25–29	25
Ratio of Fe to SiO_2	0.92	1.33	1.67	2.0

8.5.4.4 Oxidizing Smelting Processes

Nearly all pyrometallurgical copper processes are based on the principle of partial oxidation of the sulfide ore concentrates. Methods based on the total oxidation of sulfide ores with subsequent reduction to metal, avoiding the formation of copper matte, are used only rarely because of high fuel consumption, formation of copper-rich slags, and production of crude copper with a high level of impurities.

Prior to the 1960s, the most important way of producing copper was roasting sulfide concentrates smelting the calcines in reverberatory furnaces and converting the matte in Peirce-Smith converters. Since that time, the modern flash smelting process with subsequent converting has become predominant. Figure 8.9 shows the flow sheet of a modern copper smelter from concentrate to pure cathode copper, including the use of oxygen, recovery of waste heat, and environmental protection. Table 8.10 compares the important stages and processes of copper production, showing the range of the matte composition for each process.

Cost. Both capital and operating costs for copper smelters must be estimated with care because the published data vary considerably [68–69]. The costs depend on the plant location, generally increasing with

- the leanness of the raw material—the lower the copper content the higher the costs
- the price and demand for energy
- rigorous environmental protection
- inflation
- low foreign exchange rates

Table 8.10: Survey of pyrometallurgical processes for copper production [67].

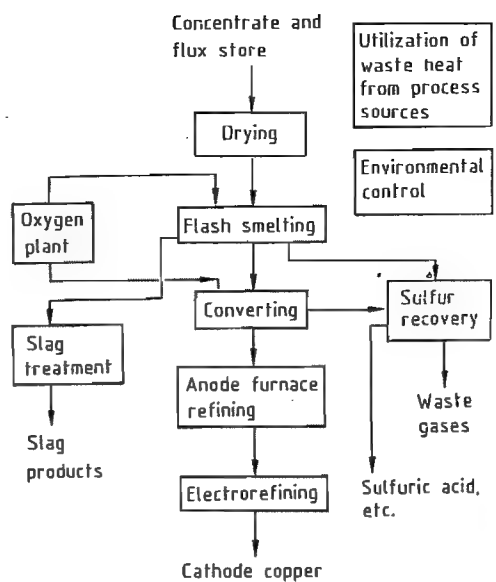
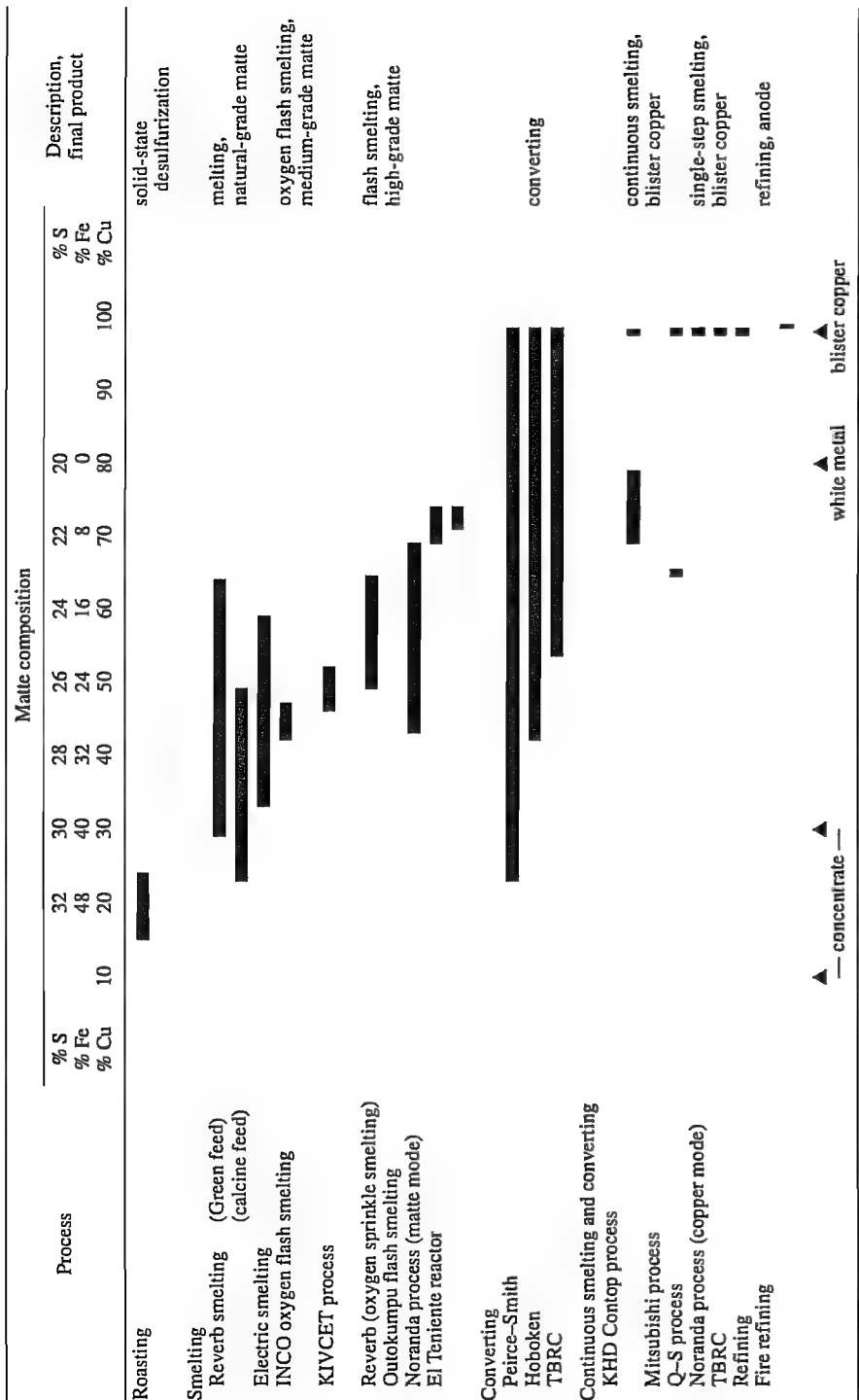


Figure 8.9: Typical flow sheet for pyrometallurgical copper production from ore concentrates [66].

The flash smelting process is the most efficient pyrometallurgical method, costing as little as one-third the conventional processes. The costs of hydrometallurgical processing also depend on the copper content, but generally the capital costs are up to 50 % lower than conventional processing.

Energy requirements have a large effect on operating costs. There are publications on comparative power demands [70–72]; however, the data vary widely and must be used with care. The step that uses the largest fraction of the energy needed to produce copper pyrometallurgically is the smelting itself [13]:

Step	Energy required per 1 t Cu, GJ	Deviation, %
Mining	5.5	35
Beneficiation	3.8	35
Smelting		
(Outokumpu flash)	8.4	20
Converting	0.0	
Anode casting	0.2	10
Electrolysis	1.3	10
Cathode casting	1.7	10
Total	ca. 21.0	

The amount of energy required to produce copper pyrometallurgically depends on the process (Table 8.11).

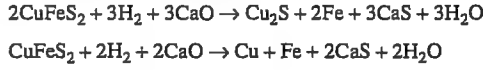
Table 8.11: Energy required for pyrometallurgical production of copper [13].

Process	Energy required per 1 t Cu, GJ
INCO Flash smelting (95% O ₂)	1.7
Electric furnace	6.7
Noranda process (30% O ₂)	6.7
Outokumpu flash smelting	8.4
Mitsubishi process	10.1
Reverberatory furnace with roasted concentrate (calcine feed)	13.4
Brixlegg process	19.3
Reverberatory furnace with raw concentrate (green feed)	21.8

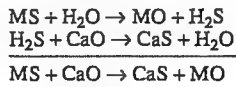
8.5.4.5 Proposals

Numerous laboratory experiments and pilot-plant runs have been carried out to develop smelting methods based on elements other than oxygen. Two lines of development have dominated reduction with hydrogen and chlorination, however, without leading to commercialization.

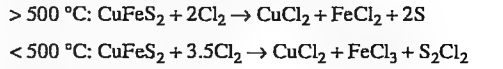
Reduction. A potential process involves the reduction of chalcopryrite [73, 74]:



The reduction by hydrogen is endothermic, but the overall reaction with calcium oxide is exothermic. A similar proposal is based on the reaction of a metal sulfide with steam in the presence of calcium oxide:

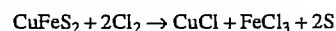


Chlorination. The reactions of chalcopryrite with chlorine are also of interest [75]:



followed by electrolysis of the molten copper(I) chloride.

The recently proposed thermoelectron chlorination process is another variation [76]:



Electrolysis. Another approach, to avoid converting, proposed the electrolysis copper matte [77].

8.5.5 Traditional Bath Smelting

At the end of the Middle Ages, copper was produced by the German or Swedish smelting process that involved roasting reduction with up to seven process steps in small shaft furnaces. Around 1700, reverberatory furnaces were constructed in which the ore was processed by roasting reaction, the so-called English or Welsh copper smelting process, originally with ten process steps.

The large blast and reverberatory furnaces of the 20th century were derived from these principles. Later, the electric furnace for matte smelting was developed.

8.5.5.1 Blast Furnace Smelting

The blast or shaft furnace is well-suited for smelting high-grade, lumpy copper ore. If only fine concentrates are available, they must first be agglomerated by briquetting, pelletizing, or sintering. Because of this additional step and its overall low efficiency, in the last decades, the blast furnace lost its importance for primary copper production and currently is obsolete and, thus, used in only a few places.

Smaller types of blast furnace, however, are used to process such copper-containing materials as intermediate products (e.g., cement copper or copper(I) oxide precipitates), reverts (e.g., converter slag, refining slag, or flue dusts), and copper-alloy scrap.

The construction of the furnace is basically related to that of the iron blast furnace, but there are considerable differences in design, especially in size and shape: the copper blast furnace is lower and smaller, and its cross section is rectangular. Recent developments in the steel industry have been adopted, including use of preheated air (hot blast), oxygen-enriched air, and injection of liquid fuels.

The furnace is charged with alternate additions of mixture (copper-containing materials

and accessory fluxes such as silica, limestone, and dolomite) and coke (which serves as both fuel and reducing agent). There are three zones in the furnace:

- In the heating zone (the uppermost), water evaporates and less stable substances dissociate.
- In the reduction zone, heterogeneous reactions between gases and the solid charge take place.
- In the smelting zone, liquid phases react.

The usual mode of operation is *reducing smelting*, which yields two main products. Sulfide ores are used to produce a matte (40–50% Cu) and a disposal slag (ca. 0.5% Cu). In contrast, oxide ores are processed directly to impure black copper ($\leq 95\%$ Cu) and to a copper-rich slag. The two ore types can be smelted together to produce matte and a slag with low copper content. Another product is top gas, which contains flue dust. Ores that contain high concentrations of arsenic and antimony also form speiss, which is difficult to decompose.

Oxidizing smelting in blast furnaces has been discontinued—not only the older processes such as pyrite and semipryrite smelting, but also the comparatively new Momoda process developed in Japan (1955) and operated in Spain (Rio Tinto) as well.

Examples of operating matte blast furnaces include Lubumbashi, Zaire; VEB Mansfeld Kombinat, Germany; Glogow, Silesia, Poland.

8.5.5.2 Reverberatory Furnace Smelting

Parallel to the increasing production of fine concentrates in the first half of the 20th century, the reverberatory furnace (reverb) became the main producer of copper matte. About 1960, there were nearly 100 large units in operation, mainly in the United States, Canada, Chile, Zaire, Zambia, Australia, Japan, and Russia. Since that time, the number has declined as a result of severe competition from modern autogenous smelting processes. The reverberatory furnace erected in Sar Chesh-

meh, Iran, a few years ago was probably the last of its type.

The largest units, with hearth areas up to 380 m², are up to 38 m long, 11 m wide, and ca. 4 m high. The construction scheme is shown in Figure 8.10. The internal furnace walls have a refractory lining of basic brick, preferably magnesite brick, for prolonged operating life; in addition, water jackets are provided for protection of sidewalls, and the suspended arch is made with exchangeable bricks. Throughput can attain 1000 t/d and consists of concentrates with fluxes (silica and limestone) and copper-rich converter slag.

The treatment of sulfide concentrates depends on the sulfur:copper ratio. If the sulfur content is too high, the material must be partially roasted to remove excess sulfur and to obtain an optimum composition for the formation of matte. This process is called a hot-calcine-charged operation. On the other hand, if the S:Cu ratio is in the proper range, no special pretreatment of the concentrate is required and the cold-wet-charged (or green-charged) operation can be used. A combined action of the two methods has been demonstrated [78].

The charge is passed into the part of the furnace near the burners, either through central or lateral openings in the roof or through the sidewalls, as shown in Figure 8.10. Fuel (pulverized coal heavy fuel oil or natural gas) and combustion air are injected at the front; the maximum flame temperature exceeds

1500 °C, and heat is transferred by radiation. In contrast to the reducing operation in a blast furnace, the reverberatory furnace atmosphere is slightly oxidizing or neutral. The off-gas (1200–1300 °C) flows through a waste-heat boiler for steam generation and then a gas purification plant.

The front part of the furnace functions as a melting zone, and the back half as a settler where matte and slag separate. The copper content of such mattes is generally controlled to 35–50%. The depth of the molten bath is generally 40–50 cm for slag and 60–80 cm for matte.

A special problem with reverberatory furnaces is the formation of high-melting magnetite, which can lead to operational problems and even furnace shutdown. Because of roasting, calcine charging produces more magnetite than does green charging.

The concentration of sulfur dioxide in the waste gases, < 1 vol% in calcine-charged smelting and ca. 2 vol% in green-charged smelting, is too low for the production of sulfuric acid.

The reverberatory process has the highest energy consumption of all proven pyrometallurgical copper matte smelting methods. A green-charged furnace consumes ca. 60% more fuel than a calcine-charged unit for the same smelting capacity, and nearly thrice the energy input of the Outokumpu flash smelting furnace.

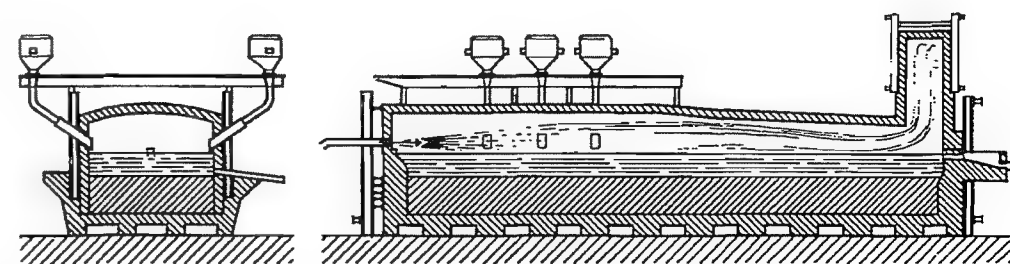


Figure 8.10: Schematic longitudinal and cross-section views through a reverberatory furnace [46].

8.5.5.3 Modern Reverberatory Smelting

Conventional reverberatory smelting is thermally inefficient and produces a large volume of low-SO₂ waste gas that is unsuitable for producing sulfuric acid. New developments derived from the principle of reverberatory smelting eliminate these disadvantages, chiefly by using oxygen and rebuilding extant furnaces. Some of these developments are the following:

- **Conventional-burner oxygen enrichment.** The improvement in efficiency is achieved by increasing the oxygen concentration in the combustion air of conventional front burners to 30–40 vol% O₂, saving energy and increasing the concentration of sulfur dioxide in the off-gas to the point that the off-gas is suitable for sulfuric acid production.
- **Oxy-fuel reverberatory smelting [79].** Special oxy-fuel burners mounted in the furnace roof fire vertically downward onto the charge with up to 60% oxygen-enriched combustion air. The smelting rate may increase to 50%, and the concentration of sulfur dioxide in the off-gas may increase to 7 vol%, adequate for producing sulfuric acid. Several plants have been built on this principle: Onahama smelter, Japan; Caletones smelter, El Teniente, Chile; and smelters in Canada and Russia.
- **Oxygen sprinkle smelting.** A recent invention [80] that involves installation of three or four sprinkler burners in the furnace roof for feeding concentrates fluxes fuel (pulverized coal) and oxygen (98%) produces a high-grade matte containing ca. 75% Cu.

While the conventional reverberatory furnace is primarily a physical melting apparatus, the new variant is an efficient chemical reactor. This operation was a transition stage to the autogenous flash smelting processes and was first employed at the Morenci smelter, Phelps Dodge Corp., New Mexico, United States.

- **Bai-Yin copper smelting process (BYCSP).** A new concept originating from the Bai-Yin Non-Ferrous Metals Co. [81], China, uses a furnace divided by a partition wall into a roasting/smelting zone and a settling zone. The molten bath is intensively agitated by air, which is blown through tuyères arranged in series. This method is said to have twice the smelting capacity of conventional operations.

8.5.5.4 Electric Furnace Smelting

In regions where relatively cheap electrical power was available, electric furnaces were built. The Scandinavian countries were the first to do electric matte smelting: 1929 at Sultjelma, Norway; 1938 at Imatra, Finland, and 1949 at Rönnskär, Sweden. Approximately 30 electric matte smelting furnaces are now in operation in Scandinavia, the United States, Canada, Zambia, South Africa, and Russia.

Electric furnaces have the rectangular ground plan and the dimensions of larger reverberatory furnaces. Along the centerline, up to six Soderberg continuous self-baking electrodes are used with alternating current (Table 8.12). The largest furnace of this type in the world, at the Inspiration smelter in Arizona, has an electrical power input of 51 000 kVA [82–83].

Table 8.12: Two examples of electric matte smelting furnaces.

Company and plant location	Electrical load, kVA	Inside dimensions, m			Hearth area, m ²	Electrodes		Furnace input, t/d
		Length	Width	Height		Number	Diameter, m	
Boliden, Rönnskär, Sweden	12 000	24	6	3	144	3	1.2	500
Inspiration, Inspiration, Arizona, United States	51 000	36	10	5	360	6	1.8	1650

The smelting process in such units is similar to the operation in reverbs, but the concentrate is usually dried–rarely roasted–before charging. The converter slag is returned to the furnace. The composition of matte and slag resembles that of the reverb products, but the content of magnetite is lower because the roasting process is omitted. No fuel is burned and the volume of waste gases and the quantity of flue dust are small. The SO₂ content of the waste gas can be 10%. The off-gas also contains carbon oxides from the consumption of the graphite electrodes.

A significant difference between the electric furnace and the reverb is the inversion of the temperature gradient in the furnace cavity. In the reverb, the combustion gases have the highest temperature, whereas in electric matte smelting, the waste gases are ca. 500 °C cooler than the slag phase, which is heated by the electric energy. Accordingly, in the electric furnace, cheap refractories are sufficient for lining the walls above the slag zone and the roof; only a common arch is required.

The temperatures of both molten phases depend on the submergence of the electrodes, and the required heat is controlled by the electrical power supplied. Heat transfer takes place chiefly by convection, which causes intense circulation in the molten bath.

The current is divided into two partial circuits, through slag and through matte. The difference in conductivity is great, slag:matte ratio of 1:102 to 1:103; therefore, the depth of immersion of the electrodes into the liquid slag must be precisely controlled. As the electrodes immerse deeper into the slag, more current flows through the matte. If they touch the matte layer, a short circuit occurs. These considerations lead to an approximate relation between the electrical power input and the depth of the slag layer: 6000 kVA and 0.5 m, 30 000 kW and 1.0 m, and 50 000 kW and 1.5 m.

The matte layer reaches a maximum height of ca. 0.8 m. The smelting capacity of electric furnaces is higher than that of reverbs, averaging 3–4 t m⁻² d⁻¹.

Brixlegg Process. Lurgi developed [84] and practiced at Brixlegg, Tirol, Austria, a modification of the old roasting reaction process. Nearly dead-roasted concentrates are reduced in batches by coal in a small special circular electric furnace (2500 kVA, 5-m diameter). The crude copper averaged only 95% Cu, and the operation has been discontinued.

8.5.6 Autogenous Smelting

Autogenous smelting involves the use of combustion heat generated by reactions of the feed in an oxidizing atmosphere in which the sulfide concentrate acts partly as a fuel. The formerly separate steps of roasting and smelting are combined into a roast-smelting process. The spatial and temporal coupling of exothermic and endothermic reactions leads to an economical process, but the sensible heat of nitrogen in the air causes a deficit in the heat balance. In practice, various measures must be taken:

- Preheating combustion air with waste heat or in a preheater
- Increasing the oxygen content of the combustion air and even using pure oxygen
- Combustion of natural gas, fuel oil, or pulverized coal in supplementary burners

To achieve autogenous operation and prevent agglomeration of the feed, the moisture in the concentrate must be removed by drying before charging. The quantity of added fluxes is minimized as far as practical to save energy.

Because the residence time of the sulfide particles in the reaction chamber is only a few seconds, kinetic conditions predominate over the thermodynamic equilibrium. The reactants form a heterogeneous system, with the feed suspended in the gas flow, thus the term smelting in suspension. These processes have several advantages:

- High rate of reaction, increasing the production rate
- Energy savings
- Low volume of off-gas and correspondingly high concentration of SO₂ and low quantity of flue dust if oxygen is used

However, a typical disadvantage is the high copper content of the slags.

8.5.6.1 Outokumpu Flash Smelting

After a preliminary test in 1946, the first full-scale flash smelting furnace was started in 1949 by Outokumpu Oy in Harjavalta, Finland. In recent years this process has partially replaced reverberatory smelting, and it will probably become the most important method in the future. At present, more than 30 Outokumpu furnaces are in operation, with a total capacity of nearly one-third of the world primary copper production. In Japan alone there are seven Outokumpu units. The Outokumpu process is easily converted to computer control [85].

Furnace Design (Figure 8.11). A flash furnace has been developed from a reverb with a mounted roaster in which smelting takes place simultaneously. Large units comprise three sections with approximate dimensions as follows:

- Circular reaction shaft for roasting and smelting dried concentrates in suspension; 6–7 m in diameter and 7–9 m high
- Settling hearth for collecting the molten droplets and separating matte from slag; 120–160 m² hearth area and up to 24 m long, 6–7 m wide, and 3 m high

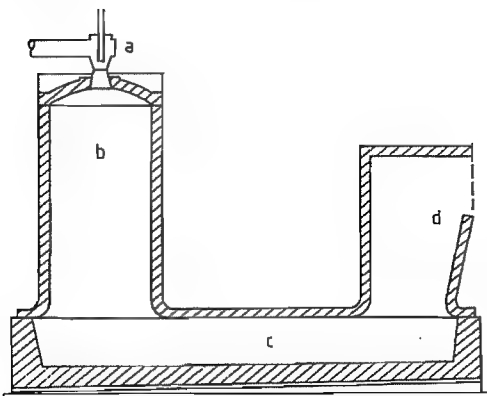


Figure 8.11: Outokumpu flash smelting furnace, longitudinal section [86]: a) Concentrate burners; b) Reaction shaft; c) Settler; d) Offtake shaft.

- Rectangular uptake shaft for waste gas and flue dust; 6–7 m long, 3 m wide, and 6–7 m high

Operation [87]. Various sorts of concentrates ($\leq 10\%$ H₂O) and a few fluxes (mainly silica) are mixed and dried in rotary dryers or in flash dryers. The dried feed is conveyed to the top of the reaction shaft, where three or four special concentrate burners are mounted. Measures required to maintain autogenous conditions include preheating of combustion air in special air preheaters up to ca. 500 °C, oxygen enrichment, and conventional burners for additional firing. The oxygen:concentrates ratio determines the final copper content in the matte. The heterogeneous mixture of gas and particles or gas and droplets remains in the reaction shaft only a few seconds before reaching the settler; the liquid matte and slag separate at ca. 1200 °C, and the matte is tapped for converting. Outokumpu mattes, which contain 50–70% Cu, result in slags that contain up to 2% Cu. Typical operating data are shown in Table 8.13.

Table 8.13: Outokumpu process, Ashio plant (Furukawa Co.), Japan [88].

	Air (21 vol% O ₂)	Oxygen-enriched air (41.5 vol% O ₂)
Concentrate throughput, t/d	440	550
Process air, m ³ /h	22 000	9600
Copper matte grade, % Cu	48	60
Heavy oil consumption, L/t	65	10
Off-gas		
SO ₂ content, %	11.5	33
O ₂ content, %	1.0	1.5
Flue dust, %	8.8	5.2
Production		
Blister copper, t/d	95	120
Sulfuric acid, t/d	250	330
Relative electric power consumption, %	100	128
Total consumption of heavy oil, %	100	35

Slag Cleaning. In practice two methods are used: froth flotation and treatment in small circular electric slag furnaces. The decision for one or the other is determined by economics. In froth flotation the slag concentrate is returned to the feed, and the tailings are dis-

carded. The second method involves the reduction of flash furnace slags in an electric furnace, which yields a matte and slag that is suitable for sale.

Off-gas and Flue Dust. The waste gases are separated from part of the flue dust at ca. 1250 °C in the offtake shaft and pass through a waste heat boiler for generating steam, and subsequently to an electrostatic (Cottrell) precipitator for separating the mass of flue dust, which is recycled to the feed. The precleaned off-gas with SO₂ content of > 8% is usually processed to sulfuric acid.

The flue dust consists chiefly of sulfates and basic sulfates of copper lead and zinc as well as some volatile compounds of arsenic, antimony, bismuth, and selenium. Repeated recycling makes it possible to enrich selected elements for later extraction. The quantity of flue dust can reach ca. 10% of the input.

In large furnaces the throughput is ca. 60 t of concentrate per hour, corresponding to a copper production of nearly 150 000 t/a.

Special Operations. There are several recent variations of Outokumpu flash smelting, especially in Japanese smelters:

- Ashio smelter (Furukawa Co.), Japan. The flash furnace has been rebuilt with the shortest reaction shaft of all Outokumpu units, only 4.7 m high, to minimize heat loss. A special burner and use of high oxygen content in the blast air compensate for this short reaction zone [88].
- Saganoseki smelter (Nippon Mining Co.), Japan. The smelter operates two Outokumpu units in which hot oxygen-enriched blast air is used. Heating of the input air to 1000–1200 °C takes place in special hot-blast stoves. The overall energy efficiency is reported to exceed that of the conventional Outokumpu process [89].
- Tamano smelter (Hibi Kyodo Smelting Co.), Japan. To eliminate the slag cleaning furnace, electrodes are inserted into the settler of the flash furnace. This mode is termed the FSFE (flash smelting furnace with electrodes) process [90]. A second

plant, the PASAR smelter, has been erected recently in the Philippines.

- Glogow smelter, Silesia, Poland. The concentrates used here have an unusual composition: 17–32% Cu, 1–3% Pb, only 2–5% Fe, 7–10% S, and even 5–8% organic carbon. Air that is highly enriched with oxygen (up to 80 vol% O₂) is used, which permits the direct production of blister copper. The two disadvantages are the high content of impurities (lead, arsenic, and bismuth) in the copper and the extremely high percentage of copper (7–16%) in the slag, both depending on the level of oxygen enrichment [91].
- Hidalgo smelter (Phelps Dodge Corp.), New Mexico, United States. This new plant is intended to produce elemental sulfur instead of sulfuric acid by reducing the SO₂ in the offtake shaft with pulverized coal and hydrocarbons [92].

Trends. The diversity of modified furnace constructions and operating methods shows the adaptability of the Outokumpu process to different raw materials and smelter locations. As increasing oxygen content has been used in the blast air, the process has approached the principle of INCO flash smelting. On the other hand, newer developments aim at the production of blister copper or white metal (75–80% Cu) from concentrates in only one vessel, thereby approaching continuous smelting and converting as in the Noranda process.

8.5.6.2 INCO Flash Smelting

INCO Metals Co., Canada, was the first company in the nonferrous metal industry to use commercially pure oxygen, which it did in autogenous flash smelting. After tests in the late 1940s, two smaller furnaces were put into operation in 1952–1953, and a rebuilt unit with a capacity of ca. 1400 t/d has been operating since 1968 [93].

The construction is similar to that of a medium-sized reverb (about 23 m × 6 m with a maximum height of 5 m), but feed and oxygen (95–98 vol%) are blown horizontally through

burners at both ends of the furnace. The offtake is arranged at the center of the roof. A sheet steel encasing keeps the furnace nearly gastight. The matte contains ca. 50% Cu and the slag 0.7% Cu.

The advantages of the process rest on the use of pure oxygen and relate particularly to handling off-gas. Because of the relatively small gas volume, the dust formation is negligible, and the cooling and dust-collecting system can be small. On the other hand, the SO_2 content of the off-gas is ca. 80%, so that liquid sulfur dioxide can be produced. Other advantages are the relatively low energy requirement and the simple design. Figures 8.12 and 8.13 give the heat balance for INCO flash smelting and a sketch of the furnace.

However, the INCO process is employed only to a small extent. Apart from an older plant in Almalyk, Uzbekistan [94], only two companies in the United States have chosen this process in recent years for modernizing their facilities: Hayden smelter (ASARCO), Arizona and Hurley smelter (Kennecott Copper Corp.), New Mexico.

8.5.6.3 KIVCET Cyclone Smelting

Developments in power-plant technology have led to adoption of the cyclone principle

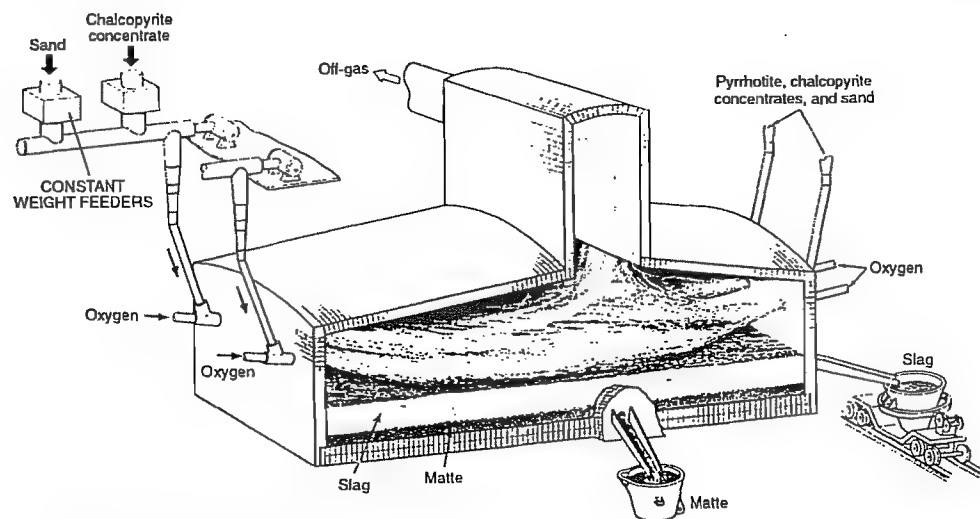


Figure 8.13: Principle of INCO flash smelting furnace.

by the metallurgical industry. The acronym KIVCET uses the initial letters of the following Russian terms: oxygen, vortex, cyclone, electrothermic. The development began in 1963, and the first plant was operated by Irtysh Polymetal Combine in Glubokoe, Kazakhstan; other ex-USSR plants are under construction [95].

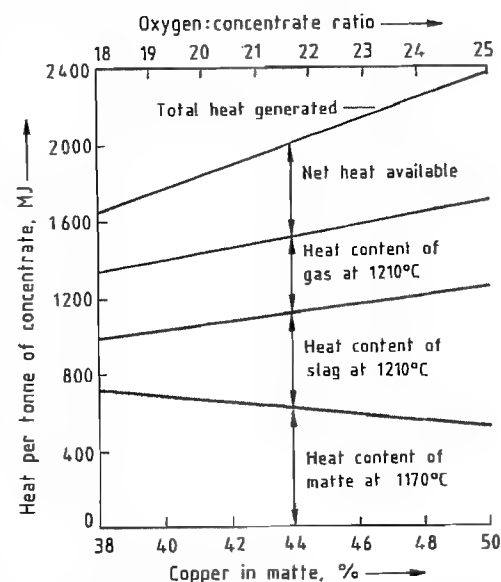


Figure 8.12: Heat balance of INCO flash smelting [93].

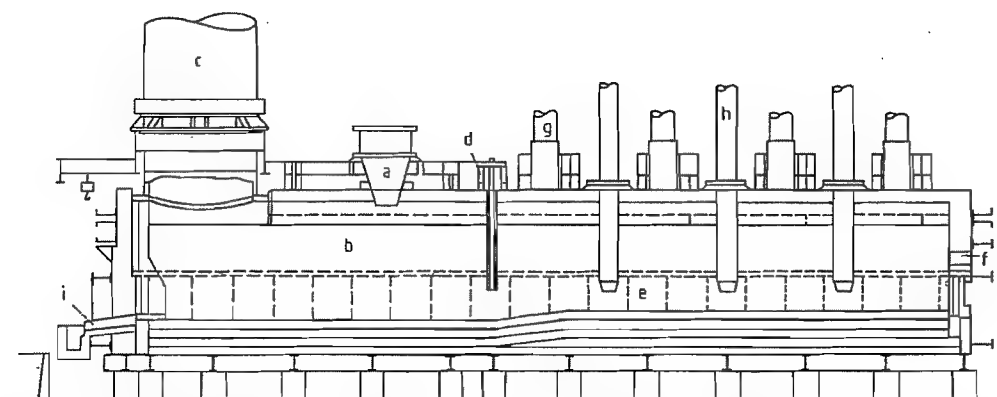


Figure 8.14: KIVCET furnace [95]: a) Smelting cyclone; b) Separating chamber; c) Cyclone waste-gas offtake; d) Partition wall; e) Settling reduction hearth; f) Slag tap hole; g) Feed of reductant and offtake for waste gas from the hearth; h) Electrical resistance heating; i) Matte taphole.

Table 8.14: KIVCET process: analysis and yield [95].

Analysis and yield	Metal		
	Cu, %	Zn, %	Pb, %
Analysis			
Concentrate ^a	25.60	10.0	1.7
Copper matte	50.00	2.5	2.0
Slag	0.35	3.5	0.2
Yield			
In matte	99.1	12.7	60.0
In oxidic condensate	—	71.0	34.1

^a Also 24.0% Fe and 33.0% S.

The method is aimed at processing copper sulfide concentrates that contain considerable amounts of other metals. The essential part of the continuously operated plant is the smelting cyclone, in which the concentrates are fed vertically, and technical-grade oxygen ($\leq 95\%$) is blown in horizontally, so that reaction takes place rapidly above 1500°C .

The furnace is divided to allow separating and settling of the reaction products, in this respect similar to a reverb. In contrast to the separation chamber, the atmosphere in the electrically heated settler is maintained in a reducing state so that the slag does not need special posttreatment.

The off-gas volume is small, and the percentage of SO_2 can be up to ca. 80%. Metals are recovered from the flue dust of both the separating chamber and the settler. Table 8.14 and Figure 8.14 explain the process.

Using a KIVCET license, KHD Humboldt Wedag AG, Köln (Cologne), is developing the combined Contop process [96] (Section on Other Processes).

8.5.6.4 Flame Cyclone Smelting

The flame cyclone reactor (FCR) process was suggested by LURGI and Deutsche Babcock AG ca. 1975 and has been demonstrated at a pilot plant of Norddeutsche Affinerie in Hamburg with a capacity of ca. 10 t/h. It is a high-temperature ($> 1500^\circ\text{C}$) reaction for autogenous smelting of copper sulfide concentrates in a high-oxygen atmosphere (up to ca. 75%). A second characteristic is the simultaneous removal of volatile compounds of other elements, such as zinc, cadmium, tin, lead, arsenic, antimony, and bismuth, as oxides and basic salts, in the flue dust. The SO_2 content of the off-gas is greater than 50%. The products are a high-grade matte containing up to 80% Cu and slag, which separates in a settler [97].

The principle of this method differs from that of the KIVCET process in that the reaction in the FCR process takes place in a special chamber situated before the cyclone, where the molten droplets are separated by centrifugal force. The process is well-suited for processing complex or dirty concentrates, the raw material of the future.

8.5.7 Converting

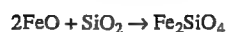
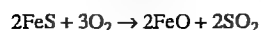
Matte produced by smelting processes is treated in the molten state by blowing with air; this stage of concentration is known as converting. Copper and iron sulfides, the main constituents of matte, are oxidized to a crude copper, ferrous silicate slag, and sulfur dioxide.

The batch converting process has been employed for many decades in two operating steps at ca. 1200 °C in the same vessel. Investigations and development of continuous methods are being made [98–99].

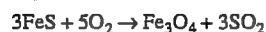
8.5.7.1 Discontinuous Converting

The conventional converting of matte is a batch process that yields in the first step an impure copper(I) sulfide containing ca. 75–80% Cu, the so-called white metal, and in the second step the converter, or blister, copper averaging 98–99% Cu. The name blister copper derives from the SO₂-containing blisters that are enclosed in the solidified metal.

First Step. The main reactions are oxidation of iron(II) sulfide and slagging of iron(II) oxide by added silica flux:

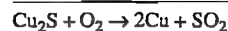
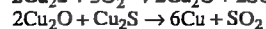
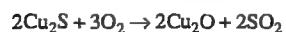


Formation of magnetite occurs near the tuyères:



In Figure 8.6, the first step corresponds to moving along the pseudobinary Cu₂S–FeS line to form an impure copper(I) sulfide.

Second Step. Continuing oxidation occurs as in a typical roasting reaction process:



In Figure 8.6 and Figure 8.15, the composition moves along the Cu₂S–Cu line from the copper(I) sulfide to crude metallic copper, the two phases being immiscible.

The blister copper contains < 0.1% S, ca. 0.5% O, and traces of other impurities.

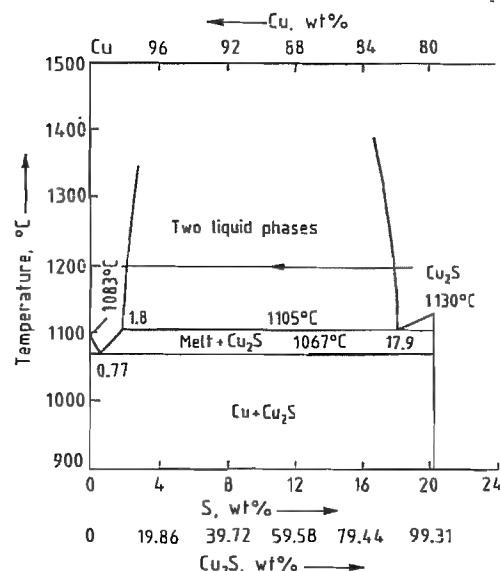


Figure 8.15: The Cu–Cu₂S system [100].

Converter Slags. The slags from the first step are iron(II) silicates (40–50% Fe) with high magnetite content (15–30% Fe₃O₄). The initial copper content of 3–8% can increase up to 15% at the end of the reaction by formation of copper(I) oxide. This slag can be decopperized by returning it to the smelting unit or by froth flotation.

The high-viscosity small-volume converter slags from the second step have a high copper content (20–40%) in the form of copper(I) oxide or silicate. When enough slag has accumulated, it is returned to the first converting stage.

Temperature. Converting is a strongly exothermic process that can overheat during oxidation of iron-rich mattes. The temperature must be held ca. 1200 °C by adding fluxes, copper scrap, precipitates from hydrometallurgical treatment (e.g., cement copper), or concentrates. The off-gas (5–8 vol% SO₂) is transferred to a sulfuric acid plant.

The blowing time per batch is a few hours; however, as the copper content of the matte increases, the converting time decreases. Occasionally, oxygen-enriched air is used to increase the throughput.

Impurities. The distribution of other elements among the phases during converting is as follows:

- Noble metals and most of the nickel, cobalt, selenium, and tellurium collect in white metal and then in blister copper.
- The bulk of zinc and some nickel and cobalt collect in converter slag.
- The oxides and sulfates of arsenic, antimony, bismuth, tin, and the basic sulfates of lead are found in flue dust.

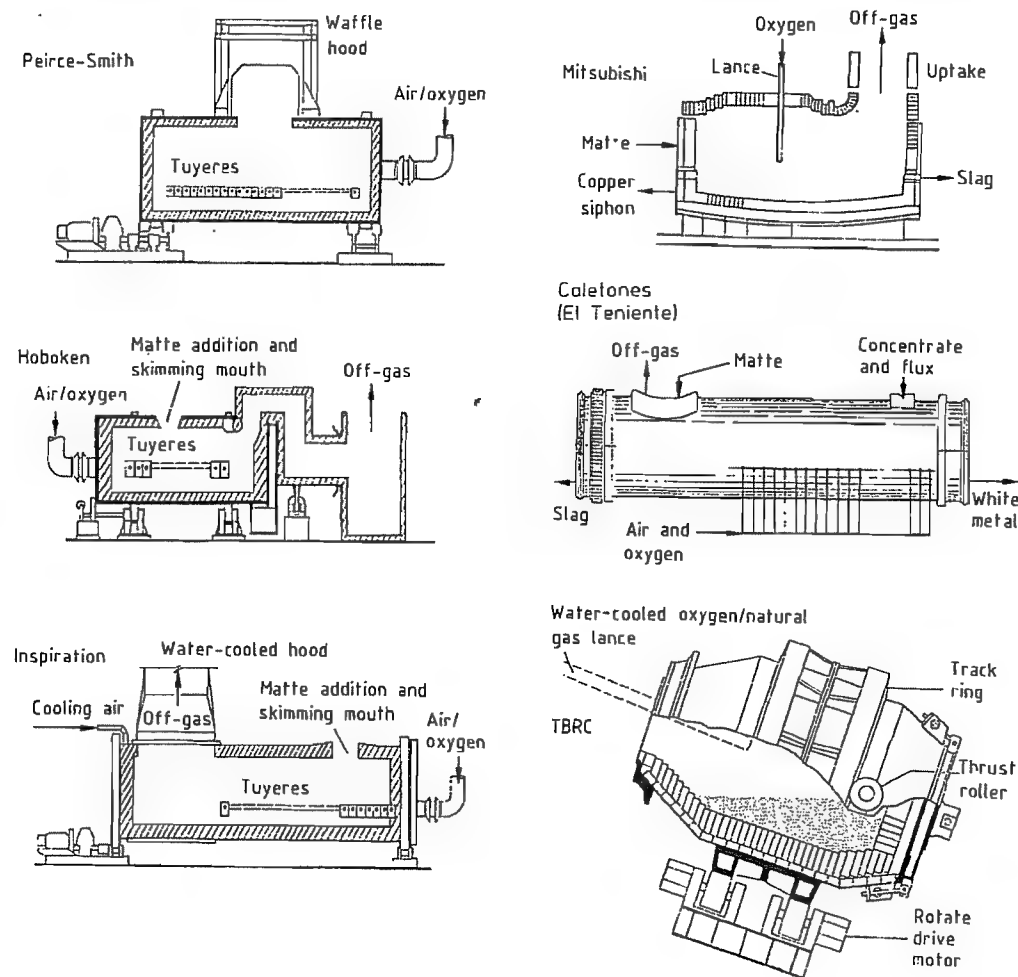


Figure 8.16: The evolution of the copper converter [101].

Converter Types. The copper converter was invented in 1880 by Manhès and David, based on the Bessemer converter, which had been used in the steel industry since 1855. This development led to the incorrect name “copper bessemerizing”, although the true Bessemer process is a refining step. Originally, the copper converter was upright, and such obsolete units were in operation until the early 1980s, e.g., the Great Falls converter developed by Anaconda Mining Co., United States.

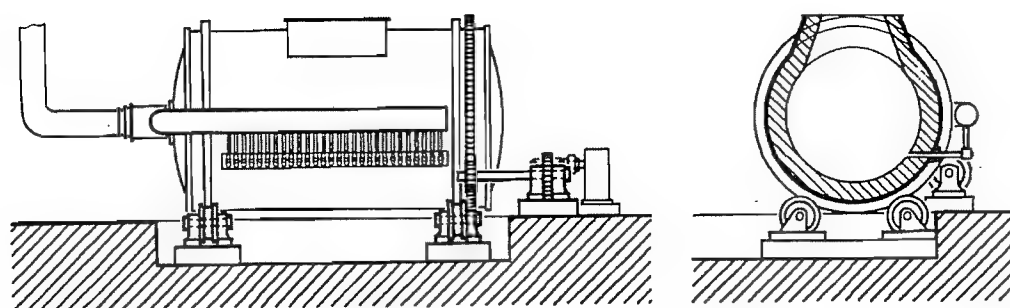


Figure 8.17: Schematic cross section and back view of a Peirce-Smith converter [45].

The following types are in use currently (Figure 8.16):

- Peirce-Smith converter. The P-S type has been the most important apparatus for converting for many decades, and the number in operation may be in the range of a thousand. It is a horizontal cylinder lined with basic bricks (magnesite, chrome magnesite) that can be rotated about its long axis (Figure 8.17); blast air is blown through a horizontal row of tuyères. In practice, the punching of tuyères with special devices is necessary to maintain the flow of air. The largest vessels are 9–11 m long with a diameter of 4–4.5 m.
- Hoboken or syphon converter [102]. This variation of the P-S type was developed years ago by Metallurgie Hoboken N.V., Belgium, but is now used by only a few smelters in Europe and in North and South America; larger units are operated at Gliogow smelter in Silesia, Poland; Inspiration smelter in Arizona; and Paipote smelter (ENAMI), Chile [103]. Its advantage is its freedom from sucking in air, so the off-gas can attain SO_2 levels up to 12%. Special features of the design are the small converter mouth and the syphon or goose neck that guides the off-gas and flue dust flow.
- Inspiration converter [104]. The construction of the Inspiration Consolidated Mines, Arizona, United States, is the most recent development in converter technology. Its design is similar to the Caletones type as it also has two mouths, the smaller for charging, the larger for the off-gas. The latter is well hooded in all operating positions.
- Caletones or El Teniente modified converter. Another modification longer than the P-S converter is the TMC [105]. The main design differences are two separated mouths for charging and off-gas flow, and the lateral tapholes for liquid slag and white metal. The latter is converted to blister copper in a conventional P-S converter. Further characteristics are testing for the direct smelting of concentrates in the converter with oxygen and the tendency to continuous operation. There are two units at Caletones smelter (ENAMI), El Teniente, Chile.
- Top-blown rotary converter [106]. The TBRC, which is known in the steel industry as the Kaldo converter, was adopted by the nonferrous industry (first by INCO, Canada) because of its great flexibility. Air, oxygen-enriched air, or on occasion, commercial oxygen is blown through a suspended water-cooled lance onto the surface of a charge of copper-containing materials. In practice, the TBRC is used batchwise for special operations on a small scale:
 - Converting copper matte with high levels of such impurities as bismuth and arsenic took place at the Tennant Creek smelter (Peko-Wallsend Ltd.), Australia, but it has been discontinued.
 - Direct smelting of concentrates (clean, complex, or dirty) to white metal or blister copper is performed at Rönnskär smelter (Boliden Metall AB), Sweden.
 - Slags from sulfide concentrate smelting and native copper are treated at Kamloops

smelter (Afton Mines Ltd.), British Columbia, Canada.

– Copper extraction from copper scrap and other secondary materials is also carried out.

- Sirosmelt process [107]. A new development, the Sirosmelt process (not shown in Figure 8.16) operates batchwise, similar to the TBRC process when used for direct smelting and subsequent converting (cf. *b*) above). Pelletized concentrates, air, and fuel are fed through a submerged lance into a special stationary furnace of circular design. After withdrawal of the primary slag, the matte is converted to white metal and then to blister copper in the same reactor. This concept of CSIRO, Australia, needs more testing before commercialization.

8.5.7.2 Continuous Converting

While continuous copper smelting processes have been in operation for many years, continuous converting of matte has come into use only slowly. In the Western world, however, these trends have recently led to a novel combination of continuous smelting and converting methods (Section on Continuous Smelting and Converting). The Eastern bloc has also been investigating continuous converting [108–109].

Among the newer concepts originating from companies in Canada and the United States is the flash converting method developed by Kennecott Copper Corp., United States [110], termed the SMOC (solid matte oxygen converting) process. Solidified matte from a smelting furnace is comminuted; the finely powdered matte is oxidized in a flash furnace with commercial oxygen to give blister copper slag, and an off-gas containing ca. 75 vol% SO_2 .

8.5.8 Continuous Smelting and Converting

Recently, copper metallurgists have tried to combine operation steps into simplified en-

ergy-saving processes. There are now two modern methods in use: the multistep Mitsubishi process and the single-step Noranda process. The Outokumpu process has recently been modified to produce blister copper [91]. Attempts have been made to employ continuous production, autogenous operation, and the use of oxygen. Apart from furnace design, the various processes differ in the following important details:

- Blowing the combustion air through tuyères into the molten bath or through lances onto the charge
- Mode of streaming of the two liquid phases (matte and slag) in unflow or countercurrent
- Method of slag decopperizing

8.5.8.1 Mitsubishi Process

Mitsubishi Metals Corp., Japan, tested the new concept in 1961 and started a commercial plant in Naoshima in 1974 with an annual capacity of 70 000 t of copper [111]. The principle of the process is the interconnecting of three furnaces, as shown in Figure 8.18:

- Smelting or S-furnace. Dried concentrates, fluxes (silica and limestone), pulverized coal, basic return converter slag, and flue dust are smelted with fuel oil and unpreheated oxygen-enriched air to produce matte.
- Slag cleaning or CL-furnace. Separation of matte from slag is effected in this electric furnace by addition of coke and some pyrite for decopperizing the slag, which is then discarded.
- Converting or C-furnace. Blister copper is produced by continuously oxidizing the high-grade matte. A special basic slag ($\text{Fe}_3\text{O}_4\text{--CaO--Cu}_2\text{O}$) is formed by addition of small amounts of limestone. This slag is returned to the S furnace after granulation.

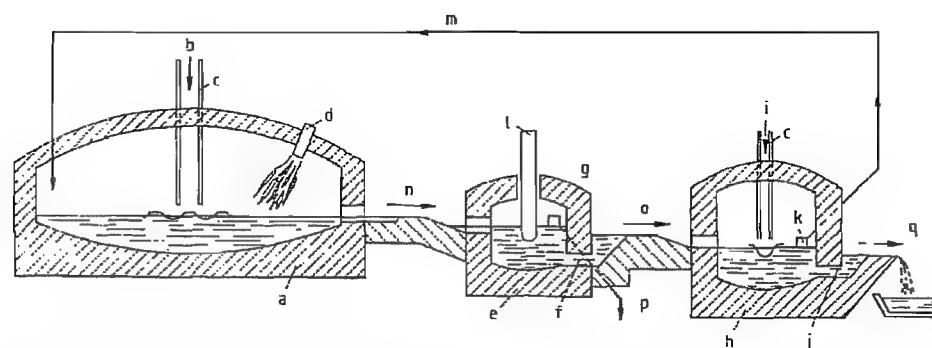


Figure 8.18: Mitsubishi process [112]. Furnaces and furnace parts: a) Smelting furnace; b) Charging part for dried concentrates and fluxes; c) Lances for blowing air and oxygen; d) Burners; e) Slag cleaning furnace; f) Matte syphon; g) Slag overflow; h) Converting furnace; i) Charging part for limestone; j) Blister copper syphon; k) Revert slag overflow; l) Anodes; m) Slag return system. Material flow: n) Matte and slag; o) Matte; p) Slag to granulator; q) Blister copper.

Table 8.15: Mitsubishi process: composition of smelting products at the Naoshima, Japan, plant [113].

Material	Composition, %					
	Cu	Fe	S	SiO ₂	CaO	Al ₂ O ₃
Concentrates	27.5	27.5	31.0	5.5	0.5	1.5
Matte	65.0	11.0	22.0			
Discarded slag	0.5	42.0	0.7	30.2	4.2	3.3
Converter slag	15.0	44.0	0.1	0.2	15.0	0.2
Blister copper	98.5		0.1			
Copper anodes	99.4					

Table 8.15 contains typical analytical data on the intermediate products. The off-gas contains ca. 15 vol% SO₂ and is used to produce sulfuric acid; the flue dust comprises 2–3% of the charged concentrates. The energy consumption is about the same as that of the Outokumpu process, but the investment and personnel costs are lower.

A new plant of this design was put into use in 1981 by Kidd Creek Mines Ltd. at Timmins smelter, Northern Ontario, Canada [114], which is to increase in capacity from 60 000 to 90 000 t/a.

8.5.8.2 Noranda Process

The tests of this first single-step continuous copper smelting process began in 1964, and a large-scale plant was put into use in 1973 at Horne smelter (Noranda Mines Ltd.) in Noranda, Quebec, Canada. The original annual capacity of 70 000 t/a has since been increased to ca. 100 000 t/a [115].

The Noranda reactor is a rotatable horizontal cylinder up to 21 m long with a diameter of ca. 5 m and lined with chrome–magnesite bricks. Its longitudinal section is shown in Figure 8.19. In normal operation the vessel remains stationary with 50–60 tuyères on a level with the molten matte. If the process is interrupted, the reactor must be revolved to raise the tuyères.

The furnace is continuously charged at one end with pellets consisting of wet sulfide concentrates ($\leq 10\%$ H₂O), silica flux, and pulverized coal. The slag is very viscous as a result of the high percentage of magnetite (20–30%) and contains 10–15% copper because liquid matte and slag move in unflow, the copper content in both phases increasing during the reaction. The slag is decopperized by flotation. The slag concentrates containing 50–55% Cu are returned to the reactor as additional feed with all flue dusts. The tailings (ca. 0.5% Cu) are discarded. Blister copper collects as a third liquid layer in the lowest part of the reactor.

The burners at both ends of the reactor are fed by gas or oil and oxygen-enriched air. The SO₂ content of flue gas is between 8 and 15 vol%, depending on the oxygen content of the combustion air and the fuel quantity.

Apart from the advantages of continuous and partially autogenous operation, the Noranda process suffers several disadvantages in its original mode:

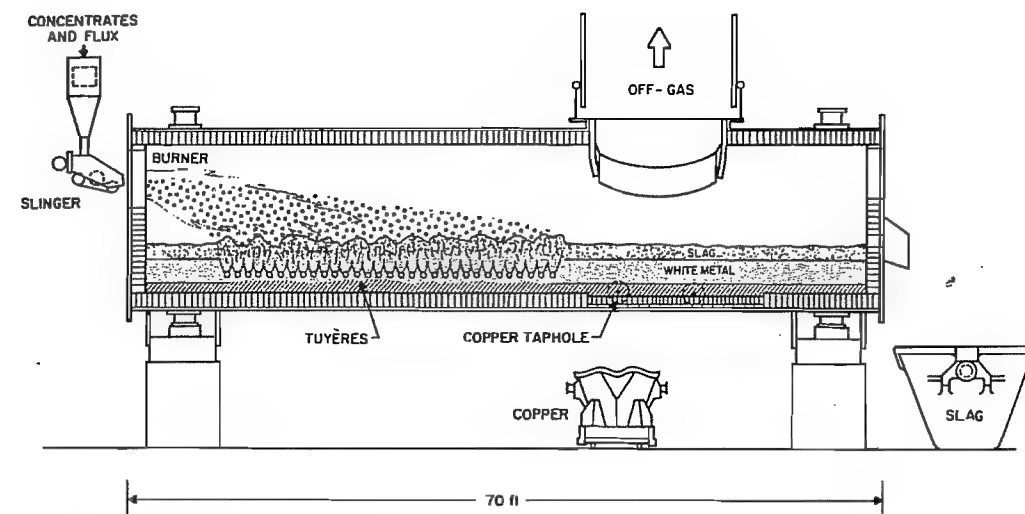


Figure 8.19: Noranda Process prototype reactor [116].

- High copper content in the slag
- High sulfur content in the blister copper (1–2%, only ca. 0.1% in batch converting)
- Large amounts of such impurities as arsenic, antimony, and bismuth in blister copper if dirty concentrates are charged

The isolated steps of conventional methods are better suited for treating ores with high levels of impurities. Therefore, the blister mode of the Noranda process was replaced by the matte mode to produce white metal, which is converted to blister copper in P–S converters. The copper content of the Noranda slag is cut in half. Table 8.16 shows the distribution of impurities in the intermediate products starting with a concentrate containing 25% Cu, 29% Fe, and 32% S.

In 1978, the Utah Copper Division of Kennecott Copper Corp. started three Noranda reactors in its Garfield smelter in Utah, United States.

8.5.8.3 Other Processes

WORCRA Process. The acronym comes from the inventor (H. K. Worner) and the company (Conzinc Rio-Tinto of Australia). In a pilot plant at Port Kembla, New South Wales, the process was demonstrated in 1968 and at-

tained a capacity of ca. 8000 t of blister copper per year. In spite of initial progress, the method was not technically successful, and the tests were dropped. However, reports in the literature [118] imply that the principle may be revived.

The process differs from the Noranda process in that the stationary furnace is U-shaped, dried concentrates are charged, and the liquid matte and slag flow in a countercurrent. The slag contains only ca. 0.5% Cu and needs no subsequent treatment. The energy consumption and the required space are greater. The principal problem was the rapid deterioration of the injection lances, which are immersed in the molten slag.

Q–S Process. A method invented by P. E. Queneau and R. Schuhmann, Jr. [119] and under development since 1981 for the extraction of lead from sulfide concentrates in a pilot plant at Berzelius Metallhütten GmbH, Duisburg, Germany, is to be tested for the production of blister copper or white metal. The Q–S reactor is similar to the Noranda design with a rotating nearly cylindrical vessel. The flow of molten matte and slag is countercurrent; thus, it produces a low-grade slag. The copper content of this slag is lowered to 0.2% Cu by a re-

ducing treatment with carbon monoxide in the same reactor, called deconverting.

KHD-Contop Process. Another recent project for the direct production of copper or lead from sulfide concentrates has been developed by KHD Humboldt Wedag AG, Köln (Cologne). The acronym Contop stands for continuous top-blowing process [120]. The process involves a series of steps in a stationary double-furnace system, each divided into several sections for different tasks. The concentrates and fluxes are continuously charged into a cyclone flash smelter resembling the KIVCET reactor, where the raw material reacts with pure oxygen at 1500–1700 °C. This heating, and slag fuming by top-blowing a mixture of pure oxygen and gaseous fuel through lances into the adjoining settling and slag cleaning reactor, remove most of the impurities by volatilization.

Thus the process provides relatively pure metal from dirty concentrates in one continuous operation. High-grade matte (75–80% Cu) flows into the second part of the reactor, which uses the HCCR process. The final product is fire-refined copper suitable for anode casting. The slag does not need posttreatment, and the off-gas can contain up to 20 vol% SO₂.

Two other proposals, the Britcosmaco process [121] of G. J. Brittingham, Australia, and the BM Autogenous process [122] of the U.S. Bureau of Mines, require special stationary furnaces in which molten matte and slag flow in a countercurrent. Tests of these processes have been discontinued.

8.5.9 Recovery of Copper from Secondary Materials

Copper is recovered from materials, including copper and copper-alloy scrap, as well as substances that contain oxidized copper, such as slag, flue dust, dross, ash, residue, and sludge.

New scrap (fabricating waste) can be recycled to the appropriate melting and casting plant. Old scrap (used copper), however, must be sorted and sampled to select the most suitable sequence of recovery operations in a smelter or refinery. The recovery of metals from copper alloys is complicated because of separation problems. In practice, pyrometallurgical treatments employing a blast furnace and converter are preferred.

Converter-Blast Furnace Method. The original so-called Knudsen process was patented in 1915 and its variants became the conventional method. Copper-alloy scrap, such as brass, bronze, gunmetal, and nickel alloys, is melted in small converters with coke and iron scrap (but no silica) during air blowing. The iron performs the three functions of reducing agent, fuel, and component for slag formation. Iron also minimizes the oxidation of copper and, thus, lowers the copper content of the nevertheless copper-rich slag. Unlike the large matte converter, the scrap converter operates under reducing conditions above the molten bath [123].

Table 8.16: Noranda process: distribution of accompanying elements in the material flow [117].

Element	Mode of operation								
	Converting to matte with atmospheric air			Converting to blister copper with atmospheric air			Converting to blister copper with O ₂ -enriched air (30 vol % O ₂)		
	Off-gas (flue dust)	Reactor slag	Matte (70% Cu)	Off-gas (flue dust)	Reactor slag	Blister copper	Off-gas (flue dust)	Reactor slag	Blister copper
Lead	74	13	13	24	74	2	21	77	2
Zinc	27	67	6	21	78.9	0.1	14	85.8	0.2
Cadmium	—	—	—	95.5	4	0.5	95	4.5	0.5
Arsenic	85	7	8	19	27	54	39	14	47
Antimony	57	28	15	29	36	35	18	52	30
Bismuth	70	21	9	52	30	18	43	42	15
Selenium	—	—	—	78	7	15	60	21	19

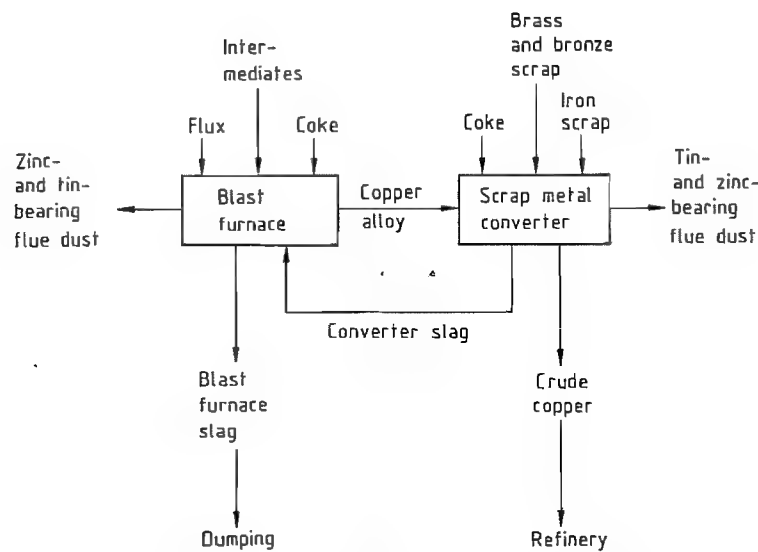


Figure 8.20: Converter-blast furnace method: scheme for the recovery of copper from scrap [123].

Zinc and tin are volatilized as zinc vapor and SnO and burn in the converter hood to ZnO and SnO₂. Lead is also oxidized, and the PbO is partly volatilized and partly collected in the slag. The volatile compounds collect in flue dust, from which they are recovered.

Crude copper in the converter contains some impurities and must be retained. The copper-rich slag must be processed by reducing blast furnace smelting to yield black copper (Figure 8.20).

Blast Furnace-Converter Method. The reversed process is well-suited for smelting oxidized secondary materials [124]. This method of processing brass scrap produces zinc oxide, which is utilized as a raw material for zinc white or zinc metal. Bronze and gunmetal scrap yield mixtures of oxides from which tin lead solder is made.

The treatment of nickel alloys (e.g., German silver, a Cu–Ni–Zn alloy) is difficult because of the tendency of nickel to form slag. Methods have been developed that let the nickel pass into the electrolyte during copper electrolysis (see Chapter 12).

Summary. There is no satisfactory general method for the processing of alloy scrap despite many proposals [125–129]. Secondary

metal reserves are becoming increasingly important, as are processes for the recovery of metals from them [130–131].

8.5.10 Hydrometallurgical Extraction

Most “new” hydrometallurgical methods are derived from well-known reactions of analytical chemistry. While pyrometallurgical processes readily handle raw materials of variable composition, hydrometallurgical methods have advantages of specific adaptability and high selectivity. They are particularly suitable for processing low-copper-content oxidized or combined oxide-sulfide copper ores, dump stocks, residues, or intermediate products.

Disadvantages are the relative slowness of leaching, the large volume of solution per unit mass of copper, and the complicated extraction of precious metals that remain in the leaching residues. Another problem is the removal of sulfur from sulfide ores. Although sulfur dioxide is not generated, dilute solutions containing sulfate ion, which must be precipitated as gypsum to avoid water pollution, are formed. Newer developments are aimed at direct separation as elemental sulfur.

Currently, ca. 15% of the primary world copper is produced by hydrometallurgical extraction. The main products are electrowon pure copper and crude cement copper.

8.5.10.1 Principles

The following is only a brief survey of hydrometallurgical processes; details are to be found in the literature, e.g., [132–133].

Basic Process Steps. Hydrometallurgical processes can generally be subdivided into the following steps:

- Pretreatment, physical (e.g., comminution) or chemical (e.g., roasting)
- Leaching, chiefly with sulfuric acid or ammoniacal solutions, sometimes under oxidizing conditions
- Solution purification, e.g., by precipitation of impurities and filtration or selective enrichment of copper by solvent extraction or ion exchange
- Separation, precipitation of copper metal or copper compounds such as Cu_2O , CuS , CuCl , CuI , CuCN , or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (crystallization)
- Posttreatment, e.g., fire-refining of crude cement copper or thermal reduction of copper compounds

Leaching. In copper production, leaching is used in a number of ways:

- In situ leaching, applied in loose ore bodies
- Dump or heap leaching of lumpy material
- Vat or percolation leaching of small-sized material
- Agitation or slime leaching of fine-grade material without pressure
- Pressure leaching of fine-grade material or without oxygen

In practice, only a few proven chemicals, *lixivants*, are used:

- Dilute sulfuric acid, suitable for leaching oxidized copper ore such as oxides, basic carbonates and sulfates, and silicates
- Solutions of iron (III) salts, especially iron(III) sulfate, as oxidizing agents in sul-

furic acid if sulfide copper minerals are also present

- Ammoniacal solutions of ammonium salts, especially ammonium carbonate for oxidized ores, as well as for native copper if the accompanying gangue is soluble in acids

Other *lixivants* have been proposed and occasionally used, e.g., hydrochloric acid, nitric acid, concentrated sulfuric acid, and solutions of iron(III) chloride, copper(II) chloride, or dichromates. In pressure leaching of sulfide ores, oxygen is advantageously applied to oxidize the sulfide to sulfate or elemental sulfur. Economic aspects are decisive for the choice of a *lixiviant*.

A recent development is the *bacteria-assisted leaching* of low-grade copper ores and industrial wastes. Certain autotrophic bacteria accelerate the oxidation of copper and iron sulfides. Typical species are *Thiobacillus thiooxidans*, which oxidizes sulfide to sulfate, and *Thiobacillus ferrooxidans*, which oxidizes iron(II) to iron(III). The $\text{Fe(II)} \rightarrow \text{Fe(III)}$ reaction takes place slowly in atmospheric oxygen, but the bacteria catalyze it.

The reaction rate depends on the living conditions of the bacteria. Bacterial leaching of sulfide copper ores is carried out at temperatures between 25 and 40 °C, pH (sulfuric acid) of 1.5–3.5, a definite concentration of metal ions, access to oxygen, and no direct exposure to sunlight.

Currently, species of bacteria can be developed and cultured for the performance of specific tasks. It seems likely that such biotechnological methods may assume increased importance because of their lack of environmental problems and their low energy consumption [134–135].

Solvent or Liquid-Liquid Extraction [136–137]. The solvent extraction of dilute copper solutions from leaching processes concentrates copper and eliminates impurities. This operation is based on the immiscibility of liquid aqueous and organic phases, with a high solubility of copper, but not of impurities, in the organic phase.

The solvent extraction process comprises two steps: selective extraction of copper from an aqueous leach solution into an organic phase (extraction circuit) and the reextraction or stripping of the copper into dilute sulfuric acid to give a solution suitable for electrowinning (stripping circuit).

There are two important groups of proven organic chemicals for solvent extraction: LIX types (Henkel Corporation, formerly General Mills Chemicals, United States) and KELEX types (Ashland Chemical, United States). The improved selectivity of newly developed reagents has increased the importance of solvent extraction.

Ion Exchange [138]. Resins for selective absorption of copper have been used only in special cases, e.g., for recovery of dissolved metals from electroplating wastewater [139].

Cementation. The reduction and precipitation of copper from dilute sulfuric acid leach solutions by iron is the oldest hydrometallurgical method. In practice, iron scrap, if possible sheet iron, or sponge iron produced by reduction of iron oxides so that a large surface area is available, is used. The precipitation is carried out in vessels such as launders, cells, tanks, and special cone precipitators [140].

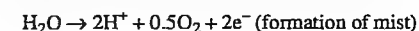
The precipitate, cement copper, is an impure copper, from ca. 60% to > 90% Cu. Further treatment is usually by a pyrometallurgical process. Relatively pure cement copper can be used as a raw material for the production of copper sulfate.

Electrowinning [141]. The electrolytic deposition of copper from its solutions differs from the electrolytic refining process in two important ways: the use of insoluble anodes instead of soluble ones and, consequently, much higher voltage (ca. 2–2.4 V), with a resultant power consumption of 2000–2600 kWh⁻¹.

The cathodic half-reaction is the same as in electrolytic refining:



The anodic half-reaction results in the generation of oxygen and hydrogen ions:



The reformed acid is returned to the leaching or the extraction circuit. Because of the insolubility of anodes, anode slime does not form.

Various types of anodes have been developed [142], e.g.:

- Lead-antimony (hard lead) anodes, the conventional type
- Chiles anodes (copper-silicon alloy), an older development from Chuquicamata, Chile
- Titanium anodes—a new type—coated with a layer containing platinum metals to decrease the high overpotential of oxygen

The use of titanium avoids the disadvantages of lead anodes. Titanium anodes have high corrosion resistance, do not contaminate copper cathodes with lead, and save energy because of the lower oxygen overpotential.

In this way, the current efficiency (usually 80–90%) can be improved. Impurities from anodes and from the electrolyte lead to higher energy consumption, secondary redox reactions, and the necessity for keeping the current density below 200 A/m². Newer developments allow the use of high current densities [143].

The electrolyte can be obtained in two ways. High-value pregnant copper solutions (containing 30–40 g/L) from agitation and pressure leaching are suitable for direct electrowinning after solution cleaning. Low-value pregnant copper solutions (containing < 10 g/L) from in situ, dump, heap, and vat leaching must be enriched and cleaned by solvent extraction.

Electrowinning plants are constructed, equipped, and operated like electrolytic refineries. Their production capacity, however, is relatively small, apart from one exception in Zambia. Several plants exist in the United States, Chile, Peru, Zambia, and Zaire.

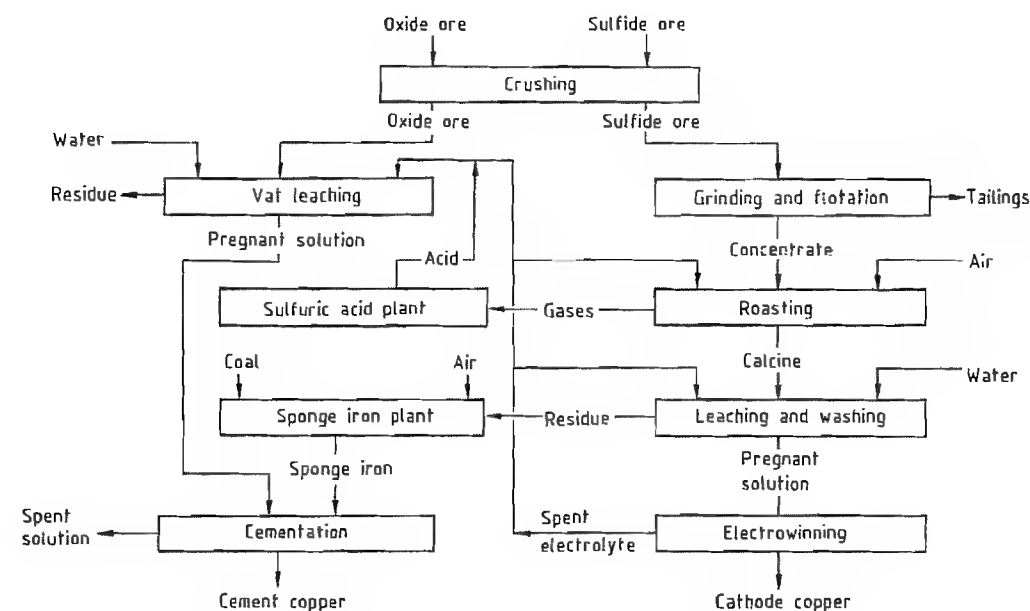


Figure 8.21: Typical flow sheet for hydrometallurgical copper production from ores [145].

Precipitation by Reducing Gases. A third way to precipitate copper from dilute solutions is reduction with gases under pressure at high temperature, usually with hydrogen, to produce metal powder. However, there is no commercial production of copper powder by this technique [144].

8.5.10.2 Processes

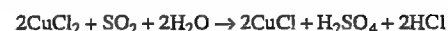
Of the great number of proposed hydrometallurgical methods, only a few have found their way into industrial practice (Figure 8.21). Numerous examples of proven and unproven processes can be found in the literature [145–147].

Processing of Oxidic Copper Ores. The most widespread method, used for many decades at Chuquibambilla, Chile, involves leaching of oxidized ores, such as copper subcarbonates, subsulfates, and silicates, in dilute sulfuric acid and the separation of metallic copper by cementation with scrap iron or by electrowinning.

A new example is the technique of the large copper oxide processing plant of the Anamax

Mining Co. at Twin Buttes, Arizona, which was started up 1975 [148]. This operation comprises ore leaching in dilute sulfuric acid, solvent extraction, and electrowinning. This succession of process steps has proven to be an advantageous combination.

Chlorine-containing oxidic ores, such as atacamite, are treated at Mantos Blancos, Chile [149], by leaching with a mixture of sulfuric and hydrochloric acids to produce a solution of copper(II) chloride, from which copper(I) chloride is precipitated by reduction with sulfur dioxide. The acid mixture is regenerated:



Refined copper is obtained from the precipitate pyrometallurgically.

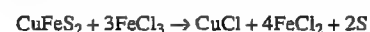
Processing of Sulfide Copper Ores. There are numerous possibilities for treating sulfide ore concentrates by hydrometallurgical methods, with or without pretreatment by roasting. The following examples of commercial processes are arranged according to the final state of sulfur (sulfur dioxide; sulfates, including

thiosulfates and dithionates, or elemental sulfur).

One of the oldest methods is the *RLE process* [145], which involves roasting, leaching, and electrowinning. After roasting concentrates in fluidized-bed reactors and generating sulfur dioxide, the calcines are leached with sulfuric acid spent electrolyte, and pure copper is separated by electrowinning. This process, developed by Hécla Mining Co., was applied at Lakeshore Mine, Arizona, and later at Chambishi, Zambia and Shituru, Zaire.

The *Arbiter process* [150] of the Anaconda Copper Co. uses countercurrent leaching of concentrates with ammonia solution under an oxygen atmosphere at low pressure and low temperature. Copper is produced by solvent extraction and electrowinning. The sulfur is recovered as ammonium sulfate, or the ammonia can be regenerated.

The *Cymet process* [151], based on recovering elemental sulfur, has been developed by the Cyprus Mines Corp. and has undergone some variations, such as combination with anodic dissolution of chalcopryrite. A preferred technique consists of leaching concentrates with an iron(III) and copper(II) chloride solution and separating solid copper(I) chloride:



The intermediate copper(I) chloride is reduced to metallic copper with hydrogen in a fluidized-bed reactor.

Another chloride leaching operation is the *CLEAR* (copper leaching, extraction, and refining) process [152], developed by the Duval Corp. at their plant in Sieritta, Arizona. The concentrate is treated with boiling copper(II) chloride solution:



A high concentration of sodium chloride is maintained to keep copper(I) in solution as a complex. Coarse copper powder is produced by electrolyzing the purified solution.

8.6 Refining

Conventional refining comprises three stages: (1) pyrometallurgical or fire refining, (2) electrolytic refining, and (3) remelting of cathodes and casting of shapes. Refining without electrolysis is adequate if the fire-refined copper has the necessary purity and if the content of precious metals can be neglected. Extremely high-purity copper is occasionally needed for research purposes; in such cases, zone melting or repeated electrolysis of cathodes is used.

8.6.1 Pyrometallurgical

Fire refining is applied to crude copper such as blister copper from converters (97–99% Cu), black copper from blast furnaces (ca. 90–95% Cu), cement copper from hydrometallurgical operations (85–90% Cu), anode scrap from electrolytic refining, and high-grade copper scrap, chiefly unalloyed wire scrap.

The refining of molten copper to anode copper for electrolysis or commercial fire-refined copper has the following functions:

- Removing impurities by slagging and volatilization with the precious metals remaining entirely in the metallic copper
- Reducing the sulfur content to ca. 0.003% by oxidation
- Decreasing the oxygen content to < 0.1% by reduction (poling) to get a flat surface as a result of the water–gas equilibrium in molten copper

8.6.1.1 Discontinuous Fire Refining

Two different furnace types are available for batch copper refining, the older reverberatory furnace and the more modern rotary furnace. The former, which resembles smaller reverbs for matte smelting from concentrates, has a capacity of 200–400 t of copper per charge and can be fed with molten or solid copper. Rotary furnaces hold up to 350 t of

molten metal per charge and are generally fed only with liquid copper. An extra melting furnace, e.g., anode shaft type, can be required for remelting of solid materials (scrap and anode rests).

Low-sulfur pulverized coal, fuel oil, natural gas, or reformed natural gas serve as fuel. The refractory lining consists of basic bricks, such as magnesite or the more spall-resistant chrome magnesite bricks.

After charging and possibly melting, oxidation and reduction stages are carried out in sequence. At the beginning of the oxidation period, air is blown into the melt, partly slagging and partly volatilizing the impurities. During this blowing step, a part of the copper is oxidized to copper(I) oxide, which dissolves in the liquid metal (Figure 8.22). If the content of Cu_2O in copper ca. 10% (corresponding to $\geq 1\%$ O), it acts as a selective oxidizing agent:

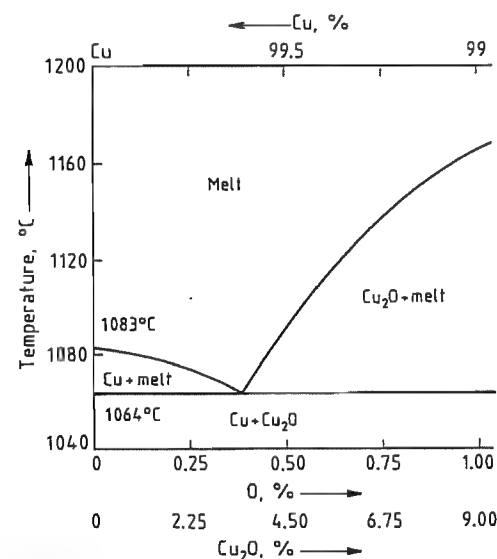
$$\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$$


Figure 8.22: Partial phase diagram of the Cu- Cu_2O system.

In practice, large amounts of SO_2 are generated so that this final stage of the oxidation period is termed boiling. Reduction of the sulfur content limits SO_2 blisters in the solid copper.

The subsequent poling with wood is a centuries-old method that is still employed in

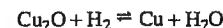
older reverb plants. Large tree trunks (poles) of beech, birch, eucalyptus, etc. are plunged under the surface of the melt to generate reducing gases and steam by dry distillation of the wood. The escaping gas mixture reacts with copper(I) oxide and mixes the molten bath [1, p. 441; 2, p. 392].

This awkward operation has been largely displaced by gas poling [153] in rotary furnaces: natural gas (CH_4), reformed gas (CO , H_2 , and N_2), propane, or ammonia [154] is blown into the copper melt through tuyères. This new process has been introduced at several large smelters in North America, Europe and Japan.

The poling operation proceeds in two steps. During tight poling, the remaining sulfur dioxide from copper(I) sulfide is almost entirely flushed out by the escaping gas a sample of liquid copper at the end of this stage solidifying without blisters or cavities. Next comes the poling tough pitch, which is necessary to reduce the copper(I) oxide and achieve the required low oxygen content. High Cu_2O content in the solidified metal causes brittleness and decreased strength; moreover Cu_2O disproportionates to copper metal and cupric ions in sulfuric acid electrolytes which disturbs the electrolytic refining operation.

The final oxygen content in fire-refined tough-pitch copper must be 0.02–0.05%; for anodes it can be 0.05–0.3%. The fire-refining process can be understood from the Cu-O system [155] (see Figure 8.22); the system Cu-O-S is important in the oxidation period (see Figure 8.5) and the Cu-H-O system for the reduction or poling period.

When a copper melt solidifies, a shrinkage of ca. 5 vol% occurs, but a flat surface can be achieved by careful control of the equilibrium



The steam of micropores can compensate the volume difference and a flat set cast is obtained.

Surface and fracture of small samples of solidified copper from the molten bath are observed during the refining process to ascertain the current state. Recently it has become pos-

sible to measure the oxygen content of the copper melt potentiometrically.

A special problem is the extremely high copper content (up to ca. 40% Cu, chiefly as Cu_2O) in refining slags. Such products are treated as high-grade oxidized copper ores.

8.6.1.2 Continuous Fire Refining

As in converting processes, the development of continuous pyrometallurgical refining has begun.

HCCR Process [156]. In the HCCR (Humboldt continuous copper refining) process, a special stationary top-blown furnace accomplishes the following functions in three sections:

- Charging or melting of solid or liquid crude copper in the first chamber
- Oxidizing the flowing copper melt by oxygen in the second chamber
- Deoxidizing the metal by reducing gases such as methane or propane in the third chamber.

All gases are blown through lances as supersonic jets onto the surface of the melt.

Contimelt Process [157]. A two-stage process for copper melting and refining was developed in 1968 by Norddeutsche Affinerie at Hamburg, in cooperation with Metallurgie Hoboken-Overpelt in Olen, Belgium. The first stage began operation in 1979, and the complete process has been operated since 1982 on a commercial scale. The continuous operations are performed successively in two units connected by launders. First is the anode shaft furnace, where charging, melting, and oxidation of crude copper take place. Second is the small drum-type furnace, where poling and casting of anodes are carried out. The oxygen content of copper from the anode shaft furnace averages 0.6%, with 0.15% after poling. A feature of the shaft furnace is the additional equipment with oxygen burners for regulating the composition of the furnace atmosphere and the overheating of copper. In comparison with conventional fire refining, the Contimelt

process provides savings in energy and labor. Increased throughput to 100 t/h is planned.

8.6.1.3 Casting of Anodes

The conventional method of producing anodes is the discontinuous casting on casting wheel machines. The pure copper molds must be sprayed with a slurry that prevents the sticking of solidified anodes; baryte, alumina, or silica flour are suitable. (Calcium-containing material is not suitable because it forms gypsum, which is partially soluble in the electrolyte.) The casting rate can reach 80 t/h. The anode weights vary between 160 and 400 kg, depending on the refinery. Anodes from modern plants usually have the following dimensions: 0.9–1.1 m long; 0.9–1.0 m wide; and 3.5–5.0 cm thick. They weigh 300–400 kg. Economic considerations call for anodes of nearly the same weight within a plant; therefore, discontinuous casting is best controlled by electronic systems.

Contilanod Process. A recent development produces uniform anodes by using the continuous Hazelett twin-belt casting system. A special method developed by Metallurgie Hoboken-Overpelt in Olen, Belgium, in cooperation with Norddeutsche Affinerie in Hamburg, is called the Contilanod process [158]. The continuous cast strip of anode copper formed between two belts and damblock chains is 1 m wide and 1.5–6 cm thick; special cutting equipment separates the strip into individual anodes 1 m long. Some refining plants use the new method, e.g., White Pine, Michigan, United States; Onahama, Japan.

8.6.2 Electrolytic

About 80% of the world copper production is refined by electrolysis. This treatment yields copper with high electrical conductivity and provides for separation of valuable impurities, especially the precious metals.

The basic patent for galvanic deposition of metals was awarded to J. B. Elkington in 1865. The most important technical problems were solved by E. Wohlwill at the Norddeut-

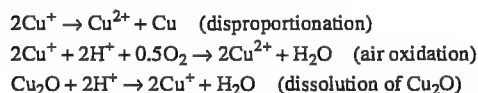
sche Affinerie in Hamburg, Germany, in 1876, and this method has been used ever since. The first electrolytic copper refinery in the United States was operated from 1883 to 1918 by the Balbach Smelting and Refining Co., Newark, New Jersey.

8.6.2.1 Principles [159–160]

Several possible half-reactions can occur at the electrodes.

Anode reactions	Cathode reactions	Standard electrode potential E^0 (25 °C), V
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.337
$\text{Cu} \rightarrow \text{Cu}^+ + \text{e}^-$	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.521
$\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{e}^-$	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.153

Secondary reactions occur in the electrolyte:



Oxidation by air and disproportionation of copper(I) ions yield a surplus of copper(II) ions in the electrolyte. The copper metal powder formed by the disproportionation of Cu^+ contributes to the accumulation of the anode slime.

The electrochemical equivalent of copper depends on the oxidation state of the copper:

Species	$\text{g A}^{-1} \text{h}^{-1}$	mg/L
Cu^{2+}	1.185	0.3294
Cu^+	2.371	0.6588

The greater electrochemical equivalent of copper(I) suggests the use of solutions of copper(I) ions instead of copper(II) ions. However, this concept has not been put into practice because of enormous industrial difficulties [161].

The two most important electrical parameters in electrolytic copper refining operations are the cell voltage and the current density. The cell voltage, which usually ranges between 0.25 and 0.3 V, is determined by several factors:

- Ohmic resistance of the electrolyte, depending on composition, temperature, electrode distance, and cell construction
- Polarization, especially concentration polarization of electrodes, which depends on the rate of electrolyte circulation
- Overpotential because of organic additives (e.g., an inhibitor for achieving uniform electrocrystallization of copper)
- Voltage loss in the circuit
- Anode passivity, which may occur at high current densities

The interaction of these effects is difficult to predict. At any particular electrolytic facility, a continuing effort is made to optimize parameters the cell voltage. The voltage loss in the conductors and contacts is minimized by good plant design and use of special contacts (Baltimore grooves, Whitehead contacts, wet contacts, etc.).

The second important parameter is the cathodic current density, which is 180–280 A/m^2 in conventional electrolytic copper refining. With increasing current density the production of copper increases and the current efficiency decreases because the cathode potential depends on the current density.

Impurities. The behavior of impurities depends on their position in the electrochemical series: elements more electropositive than copper are insoluble, while less electropositive ones dissolve in or react with the electrolyte. For that reason, the anode material is distributed by electrolysis among three phases: cathode copper, electrolyte, and anode slime (Table 8.17) [162].

Copper Cathodes. Cathode copper is produced currently in a purity between 99.97 and 99.99%. Silver can be deposited in traces; however, this can be avoided by precipitating the silver from the electrolyte with chloride ion. Other impurities, such as suspended slime or droplets of the electrolyte, may be mechanically occluded. The following measures are taken to produce copper of high purity:

- Maintenance of the optimum current density, to prevent cathodic deposition of other elements (e.g., arsenic)
- Addition of organic inhibitors to avoid the formation of nodules on the cathode surface
- Removal of impurities such as arsenic, antimony, and bismuth from the electrolyte by adsorption or chemisorption
- Prevention or elimination of suspended slimes by regulating the electrolyte flow and occasionally filtering it.

Table 8.17: Electrolytic copper refining: distribution of elements in cathodes and electrolyte [162].

	Anode, % ^a	Cathode, ppm [*]	Electrolyte, g/L
Cu	99.5	99.99%	45
Au	25.5 ppm	0.1	
Ag	399 ppm	5.0	
Pb	0.076	1.3	
Zn	0.001	0.3	0.43
Fe	0.025	2.4	0.92
Ni	0.070	0.7	16
Se	0.030	0.4	
Te	0.006	0.3	
As	0.044	0.4	3.58
Sb	0.011	0.8	0.34
Bi	0.006	0.3	0.1
Sn	0.002	0.4	0.001
S	0.007	4	
Insolubles	0.020	—	
H_2SO_4	—	—	200

^a Unless otherwise stated.

Electrolyte. The composition of copper electrolytes from various plants is generally similar: ca. 35–45 g of copper and 150–220 g of sulfuric acid per liter at an operating temperature of 55–65 °C (see Table 8.17). As a result of secondary reactions during electrolysis, the concentration of copper(II) ions increases slowly; therefore, this copper surplus must be recovered by cathodic deposition in a few (ca. 2%) liberator cells equipped with insoluble anodes, usually of antimonial lead. Soluble impurities, such as iron, cobalt, zinc, manganese, most of the nickel, and some arsenic and antimony, are also enriched in the electrolyte.

The upper limits of impurity content are ca 10 g/L for arsenic and 20–25 g/L for nickel. Part of the electrolyte is withdrawn continuously from the circuit for purification, and the volume is compensated by adding sulfuric

acid and cathode wash water. There are two methods of purification. In the first, the solution can be completely decopperized in a system of special liberator cells with insoluble anodes; arsenic and antimony are almost completely deposited and returned to pyrometallurgical operations. The electrolyte is then concentrated by vacuum evaporation to yield concentrated sulfuric acid and crude nickel sulfate, from which pure nickel sulfate or nickel metal can be produced.

The second method of purification is by producing copper sulfate. For this purpose, the sulfuric acid is usually neutralized by addition of copper shot in the presence of air. The copper sulfate is obtained by crystallization, and the mother liquor is cemented with iron scrap.

Anode Slimes [163–164]. The content of insoluble substances is < 1% of the anode weight, and they collect on the bottom of cells as anode slime. They contain precious metals (silver, gold, and platinum); selenides and tellurides of copper and silver; lead sulfate; stannic [tin(IV)] oxide hydrate; and complex compounds of arsenic, antimony, and bismuth (the undesired floating slimes). The main component is copper. In addition, gypsum and silica, alumina, or baryte from anode casting are present.

The distribution of the elements (in %) varies over wide ranges:

copper	20–50
nickel	0.5–2
lead	5–10
arsenic	0.5–5
antimony	0.5–5
bismuth	0.5–2
selenium	5–20
tellurium	1–4
silver	≤ 25
gold	≤ 4

Although the separation techniques differ greatly from plant to plant, anode slimes are generally treated as follows:

- Oxidizing leaching of copper with dilute sulfuric acid
- Recovery of selenium and tellurium by pyrometallurgical or hydrometallurgical methods

is easily removed from the steel sheets, which are equipped with special plastic edge strips. The flat and stable sheets allow close spacing between the electrodes, thereby decreasing the electrical resistance in the cell and lowering the energy consumption. The ISA system is also used at the White Pine refinery, Michigan, United States.

8.6.3 Melting and Casting

Copper cathodes must be remelted and cast to shapes because the structure of copper formed by electrocrystallization is not suitable for working to semifinished products. Cathodes are remelted in several types of special furnaces that perform the tasks of melting, postrefining (if necessary), holding, and casting. Casting can be carried out by the older discontinuous methods or by modern continuous casting.

8.6.3.1 Remelting of Cathodes

There are various kinds of furnaces that use either fossil fuels (coal, coke, fuel oil, natural gas, or reformed natural gas) or electric energy:

- Small coke-fired crucible furnaces
- Gas- or oil-fired rotary furnaces
- Large hearth furnaces (reverbs)
- Electric-arc furnaces
- Low-frequency induction furnaces
- Cathode shaft furnaces (e.g., ASARCO type)

Copper ready for pouring must be nearly free of sulfur, at most 10–3% (10 ppm) S, because a higher content affects detrimentally the mechanical properties of the metal.

In practice, copper is treated in two ways:

- After melting cathodes with sulfur-containing fuels, the copper melt must be fire-refined like blister copper, by oxidation and poling. This is the case when hearth furnaces are employed for casting wire bars.

- Use of electric power or sulfur-free fuels allows the use of continuous units, such as induction or ASARCO furnaces.

The ASARCO shaft furnace, constructed by American Smelting and Refining Co. [178–179], has a cylindrical shaft consisting of a steel jacket with a brick lining. Cathodes are charged near the top, and the combustion gases ascend in countercurrent now from groups of burners; the liquid metal is collected in a holding furnace. Apart from its effectiveness and high productivity, a distinct advantage is the maintenance of a constant, slightly reducing atmosphere by automatic control. The largest types (1.8 m diameter and 8 m high) can have a throughput up to 80 t/h. Worldwide ca. 200 units are in operation.

8.6.3.2 Discontinuous Casting

The discontinuous casting of various shapes on horizontal casting wheels with open ingot molds, analogous to the casting of anodes, was formerly the most important casting method. It is being replaced by continuous casting processes.

The capacity of the largest casting wheels is nearly 100 t/h. They are usually operated in combination with large hearth furnaces holding up to 650 t of liquid copper. The molds consist of pure copper, usually sprayed with a bone ash slurry to avoid sticking. The major product is still the 90–136 kg horizontally cast wire bar [180], or occasionally ingots and ingot bars.

8.6.3.3 Continuous Casting

Since the end of World War II, several continuous casting methods have been developed. A comprehensive synopsis, including patents, has been published [181].

Continuous casting has several technological and economic advantages over the older casting processes, such as excellent surface quality, uniform grain structure without blisters and shrinkage cavities, and energy savings.

The principle is simple, but actual practice proved difficult. Molten copper flows continuously into a relatively short water-cooled chill, usually lined with graphite and open at both top and bottom. The solidifying metal itself forms the lower closure. The shape is steadily withdrawn by clamping rolls and cooled by spraying with water.

There are three main continuously cast shapes: circular billets with a diameter up to 500 mm (for extrusion presses or tube rolling mills), square bars, and rectangular cakes with cross sections up to 1200 × 200 mm (for rolling to sheets and strips). Seamless tubes and other hollow shapes are occasionally produced. Continuous casting shapes are automatically sawn off by flying saws when they reach the required lengths (up to 6 m). In semi-continuous casting, the process must be interrupted, but the shapes can be up to ca. 12 m long.

The kind of chill is generally independent of the furnace: the liquid metal stream free-

falls into the chill (e.g., Junghans system), or the less frequent fixed connection of chill with the furnace (e.g., ASARCO casting system).

Recent methods employ a joint moving in unison with the solidifying metal and a mold with traveling parts forming a gap of the required cross section. (An example is the Hazlett process employed for continuous casting of anodes. Such casting methods are particularly suitable for continuous production of shapes with a small cross section.)

8.6.3.4 Continuous Rod Casting and Rolling

The continuous production of cast and rolled wire rod [182–183] involves considerable energy savings because the solidified hot metal can be rolled immediately. Several plants use such a direct process starting from molten electrolytic tough-pitch copper. Worldwide > 100 plants are in operation, using the following systems:

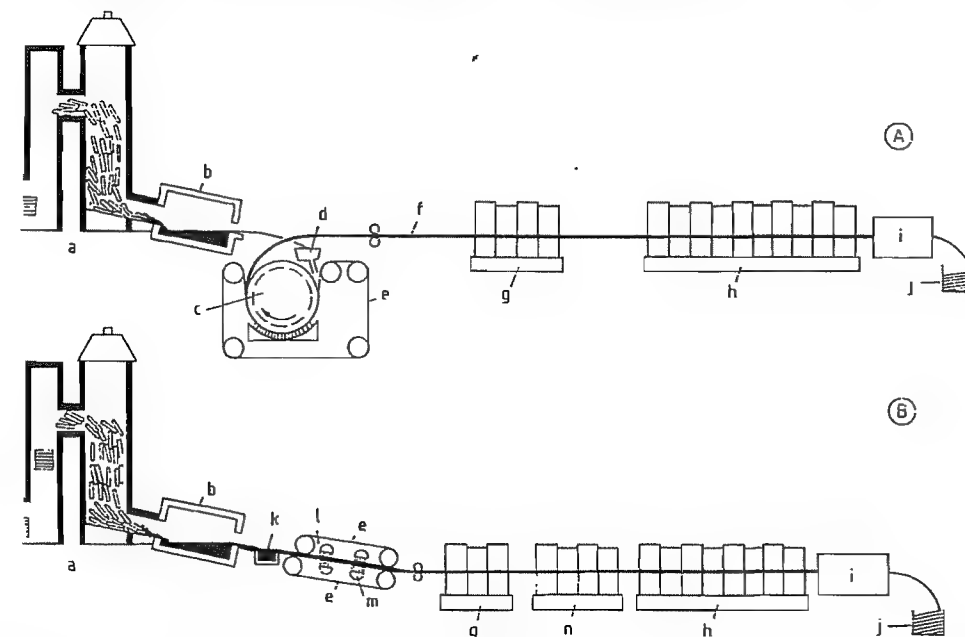


Figure 8.24: Scheme of continuous rod casting and rolling [186]. A) Southwire process; B) Contirod process. a) Melting furnace (ASARCO); b) Holding furnace; c) Wheel; d) Tundish; e) Steel band; f) Continuously cast copper bar; g) Preliminary rolling mill train; h) Finishing rolling mill train; i) Pickler; j) Coiler; k) Casting receptacle; l) Casting canal; m) Stationary edge dams; n) Middle rolling mill train.

- Properzi process [184]. The first continuous copper rod caster was constructed in 1960 following developments for other nonferrous metals. It operates on the wheel-belt casting principle, i.e., casting into the gap between the periphery of the casting wheel and the closing steel belt. About ten plants are in operation with a capacity up to 30 t/h.

- Southwire process [185]. Started in 1963 as a further development of the wheel-belt casting principle with capacity up to ca. 50 t/h. the Southwire process directly introduces the continuous cast bar into the rolling mill (Figure 8.24). After rolling, the rod, which is oxidized on the surface, is continuously treated by pickling with dilute sulfuric acid, water or steam rinsing, and wax coating. The saleable product (8–16 mm diameter) is formed into “coils” of up to 5 t, which are packaged. About 30 plants exist at present.

- Secor process [187]. Only two factories (Australia and Spain) use this modified wheel-belt casting concept, dating from 1975, with a capacity up to ca. 10 t/h.

- Contirod or Krupp-Hazelett process [188]. As a variant of the Hazelett twin-belt process similar to the Contilano process (Section on Casting of Anodes), the continuous cast bar solidifies between two belts and damblock chains and is directly moved to the rolling mill (Figure 8.24). Metallurgie Hoboken-Overpelt, Belgium, developed this system in the 1960s; the capacity of the largest units is ca. 50 t/h. At present ca. 16 plants are operated.

- General Electric dip forming process [189]. A process based on the “candlestick” principle has been operated since about 1970. A copper core rod is pulled upward through liquid copper so that its diameter increases, the thickened rod moves immediately to rolling. Oxygen-free copper can be produced by using a reducing atmosphere. The capacity is ca 10 t/h. Nearly 20 plants exist at present.

- Outokumpu up-cast process [190]. A new upward casting system developed in 1969 draws copper upward through a vertical die cooler with a cooled graphite mouthpiece dipping into the melt. The caster, comprising 8 or 12 strands, yields oxygen-free copper at the rate of ca. 2 t/h per line. Because of the small cross section (8–25 mm diameter), hot rolling is not required. Approximately 20 plants are in operation.

8.6.4 Copper Powder

Copper and copper-alloy powders are required for products prepared by powder metallurgical techniques, including friction materials, carbon brushes, self-lubricating bronze bearings, special filters, and other sintered components.

The principal methods for producing copper powders are electrolytic deposition at high current densities and the atomization of molten metal, the latter more for copper-alloy powders. Copper powders are also formed by cementation or by pressured precipitation from aqueous solutions, but such precipitates are of little commercial interest.

Atomizing is done by spraying a melt into a pressured air or water flow. Various grain shapes are formed, depending on the cooling rate and on additives that change the surface tension. Additives that decrease surface tension, e.g., magnesium, form irregular powders; those that increase it, e.g., lead or phosphorus, yield globular particles. Spongy powders can be obtained by reduction of oxidized copper powders with hydrogen.

Electrolytically deposited powder particles have dendritic shape; a typical flow sheet is shown in Figure 8.25. For this purpose electrolysis is used as a shaping process rather than for refining because high-purity copper cathodes are the anodes. The main parameters of powder electrolysis are, as Figure 8.26 shows, the following [191]:

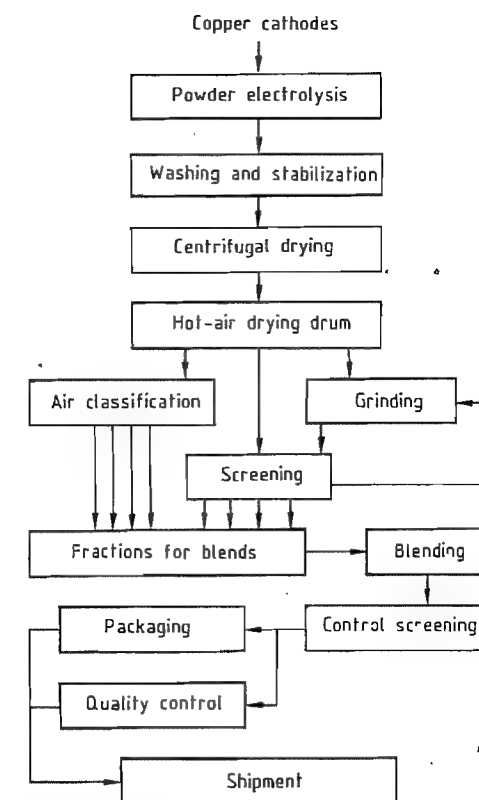


Figure 8.25: Flow sheet for electrolytic copper powder production [191].

- Cathodic current density
- Electrolyte temperature
- Concentration of copper(II) ions
- Concentration of chloride ions

Varying these reactors markedly change particle shapes and apparent densities.

Anodic and cathodic current densities differ. The former is normally 300–600 A/m², and the latter is 2000–4000 A/m², which is 10–20 times higher than the cathodic values in conventional electrolytic copper refining. This effect is obtained by using copper rod cathodes and platelike anodes. The energy consumption in powder electrolysis averages nearly 2 kWh/kg⁻¹. The powders are generally posttreated for various purposes. Electrolytic copper powders are characterized by dendritic particle shape, high purity, low oxygen con-

tent, favorable resistance to oxidation, and good green strength.

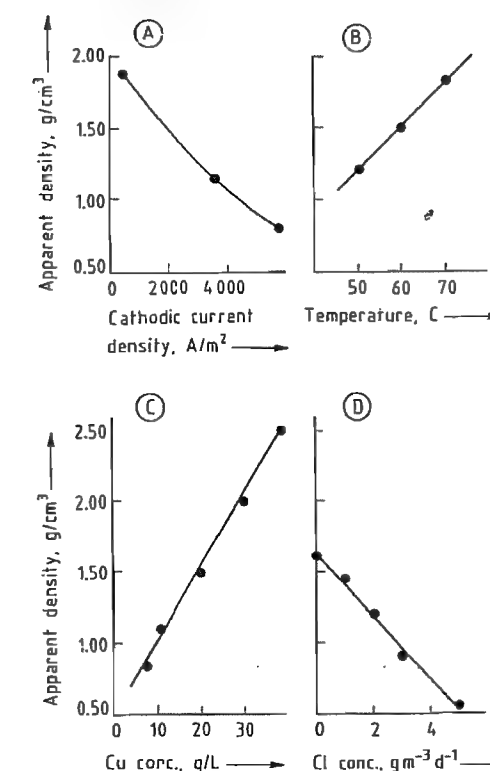


Figure 8.26: Apparent density of electrolytic copper powder as a function of four electrolysis parameters [191]. Other conditions: A) Cu 6 g/L, no Cl, 60 °C; B) Cu 17 g/L, no Cl, 3600 A/m²; C) no Cl, 50 °C, 3600 A/m²; D) Cu 13 g/L, 50 °C, 3600 A/m².

8.6.5 Copper Grades and Standardization

The three main grades of refined copper are (1) tough-pitch copper, (2) de-oxidized copper, and (3) oxygen-free copper.

- **Tough-pitch copper** normally contains 0.02–0.04% (as Cu₂O) and ca. 0.01% total of other impurities. This grade is easily worked and has an electrical conductivity of ≥ 100% IACS, but it is unsuitable for welding and brazing because of the danger of hydrogen embrittlement. About 80% of the world production of refined copper is tough pitch,

mostly electrolytic tough-pitch copper (ETP).

- **Deoxidized copper**, with no oxygen content is produced by addition of nonmetallic or metallic reducing agents, usually copper phosphide. As a result of the absence of oxygen, hydrogen embrittlement cannot occur, and such copper is well suited for welding and brazing. The content of residual phosphorus, however, increases the electrical resistivity. Deoxidized copper with low residual phosphorus (DLP, ca. 0.005 % P) is required if the metal is to be used as a conductor. Copper with high residual phosphorus (DHP, ca. 0.04 % P) can be employed for nonelectrical purposes.
- **Oxygen-free (OF) copper** is a special quality produced by keeping oxygen away from the copper melt in a controlled atmosphere. Copper of this type with an oxygen content less than 0.001 %, is suited for purposes requiring weldability and high electrical conductivity, especially electronics. OFHC, oxygen-free high-conductivity copper, is internationally known.

Standardization [14, 192–193]. Most industrial countries have established standards for copper; these national specifications include detailed specifications for chemical composition, physical properties, and geometrical dimensions, but differences exist. Table 8.18 indicates the rough equivalent between international and some national specifications for the most important copper properties.

Table 8.18: Comparison of international and selected national standards [14].

Germany DIN 1708 DIN 1787	International ISO R 1337	United States ASTM B 224	Great Britain BS 2872, etc. ^a
KE-Cu	Cu-CATH	CATH	
E1-Cu 58	Cu-ETP	ETP	C 101
E2-Cu 58	Cu-FRHC	FRHC	C 102
E-Cu 57	Cu-FRHC	FRHC	
F-Cu	Cu-FRTP	FRTP	104
OF-Cu	Cu-OF	OF	C 103
SW-Cu	Cu-DLP	DLP	
SF-Cu	Cu-DHP	DHP	C 106

^a Also BS 1036, BS 1037, BS 1038, BS 1172, and BS 1861.

8.6.6 Quality Control and Analysis

Tests for quality control of copper are carried out on samples of both refinery shapes and semifinished products. There is need to standardize the testing methods, but currently only some of them are fixed in national specifications. The most important tests are the measurement of electrical conductivity, mechanical properties, and quality of the metal surface.

The electrical conductivity is very sensitive to impurities and crystal lattice imperfections. Mechanical tests measure hardness, tensile strength, elongation at failure, and torsional fatigue strength. The spiral elongation test [194] is a complicated test method that assesses the purity and the mechanical behavior of the sample. Defects on the surface and subsurface can occur in various forms, e.g., folds, splashes, cracks, inclusions, and voids. The voids are caused by gas porosity, shrinkage porosity, and shrinkage cavities.

Nondestructive testing procedures, such as radiography, ultrasonic examination, or eddy-current technique can be used. Metallographic methods (polishing and etching) give information by microscopic examination.

Analytical methods are of interest for determining the impurity level of copper products. Both wet chemical procedures and physicochemical procedures, such as atomic absorption spectrometry, optical emission spectroscopy, and X-ray fluorescence spectroscopy, are employed, the latter essentially for quick analysis of solid and liquid co- and byproducts [195–196]. The classical analytical methods are gradually being superseded by the modern automatic instrumental techniques. It is especially important to analyze the oxygen content, and one effective modernized method is available, hot extraction, i.e., melting a copper sample in a small graphite crucible and determining the CO formed by IR absorption spectroscopy.

8.7 Processing

The pure metal produced in refineries or melting plants is manufactured into semifabricated products.

8.7.1 Working Processes

Usually copper is treated initially by non-cutting, shaping processes to obtain semifinished products or “semis”. These processes are subdivided into hot working, cold working and, if necessary, process annealing.

Hot working means plastic forming above the recrystallization temperature. Generally copper is preheated to 800–900 °C, and the subsequent hot forming is finished at ca. 400 °C. Cast bars from modern combined continuous casting/rod-rolling systems already have sufficient temperature, thus saving thermal energy. After cooling, the hot-worked copper is soft copper. Its mechanical and electrical properties are scarcely changed, but its density has increased to nearly 8.9.

The next step is cold working, which involves plastic forming below the recrystallization temperature. In practice, the operation is done at room temperature. Unlike hot working, this procedure entails an essential strain hardening of the metal by increasing the number of lattice defects; however, simultaneously formed lattice voids cause a considerable decrease of electrical and thermal conductivity. After cold working, the metal is hard copper.

Process annealing is a heat treatment that is necessary if the hardened copper must be softened again, either for continued working or for producing (soft) copper with high electrical conductivity. Special furnaces are used for the purpose of steady heating and cooling of the metal—often in a nonoxidizing atmosphere. To achieve the intended microstructural change, the recrystallization temperature of 200–300 °C must be exceeded: in practice, the metal is heated to 400–500 °C for accelerated recrystallization. Copper products with exactly defined properties can be obtained if all annealing conditions are carefully controlled.

The engineering techniques are versatile. The following working methods are of special importance:

Hot working	Cold working
hot rolling	cold rolling
extrusion	cold drawing
drop forging	cupping

Foils only ca. 0.002 mm thick are manufactured by rolling, and wires to 0.004 mm diameter by drawing. Many products of varying size are fabricated by modern variants of the extrusion process [197]. The fabrication of tubes is also quite diverse [198]. The most widely used working processes are compiled in Table 8.19.

Table 8.19: Important fabricating processes for copper products.

Refinery shapes	Hot-working process	Cold-working process	Semi-finished products
Cakes	hot rolling	→ cold rolling	sheets/strip
Wirebars or square bars	hot rolling	→ wire drawing	wires
Billets	extruding	→ cold drawing	tubes/pipes
Billets	extruding or hot rotary piercing	→ cold drawing or cold pilger rolling	tubes/pipes

8.7.2 Other Fabricating Methods

In many cases, machining operations are required, e.g., cutting, turning, planing, drilling, and sawing. However, these are more important for copper alloys than for pure copper because of copper's tendency to gum. Non-continuous casting processes are likewise more suitable for copper alloys because copper has a disadvantageous coulability. These include sand mold casting, permanent mold casting, gravity die casting, pressure die casting, and centrifugal casting. Continuous or semicontinuous casting processes, however, are well-suited for pure copper.

Galvanoplasty is an electrolytic operation for manufacturing complicated objects that require high precision and flawless surfaces such as hollow bodies, disk matrices, and elec-

trotypes. A special galvanic method is copper plating, which involves electrolytic deposition of a thin layer of copper on another metal either for surface protection or as a base layer for electroplating with another metal.

Powder-metallurgical techniques are used primarily for the mass production of small pieces, especially intricate forms such as electrotechnical and mechanical structural parts. The metal powders are first compacted by pressure and then sintered in a controlled atmosphere. The copper powder is often mixed with other powdered metals, including those that do not form common copper alloys.

There are other important fabricating methods [199]. Joining is usually carried out above room temperature by soldering, brazing, or welding. Soldering may be used for all sorts of copper, owing to the low temperature. However, welding and brazing are feasible only with deoxidized or oxygen-free copper.

When tough-pitch copper is heated in an atmosphere containing hydrogen, the steam generated collects within the grain boundaries at high pressure and can destroy the grain structure by forming cracks. This phenomenon is known as "hydrogen embrittlement".

Mechanical joining and metal bonding are also possible ways of joining copper with other materials.

Surface treatment of copper is a group of operations for surface protection or surface refinement. These include mechanical, electrical, or electrochemical handling, e.g., polishing, matte finishing, pickling by dilute sulfuric or nitric acid, metal coating or electroplating (with nickel, nickel and chromium, tin, silver, gold, or platinum metals), lacquering or coating with synthetic plastics (mainly for electrical insulation), enameling of objects (applied art), and chemical or electrochemical coloring (decoration). Coloration is effected by chemicals, mostly specially formulated metal salt solutions which form thin layers of insoluble green, red, brown, or black compounds.

8.7.3 Uses

Copper is a useful material with a wide range of applications because of its combination of properties. Because of its excellent electrical conductivity, it is the dominant conductor material. Copper is used primarily as round wire or rods, bare or insulated, for current generation, transmission, and conduction; various sorts of cables are produced for special applications. Substantial quantities of copper are made into generators, motors, transformers, and other electrical appliances. About 50% of the world consumption of copper is for electrical purposes. As a result of its high thermal conductivity, copper is well-suited for vessels and pipes, especially for heating, cooling, and heat exchange.

While high-conductivity copper is required for electrotechnical and electronic uses, special copper qualities are chosen for other uses. About 30% of world copper production is used for alloying. Copper alloys are usually cold-worked; only ca. 10% of them are cast.

Copper is frequently used in the chemical and food industries because of its high resistance to corrosion. There is substantial use of copper in mechanical engineering, by fabricators of precision implements, in vehicle construction, and in ship building. There is increasing interest in copper building construction as a material for installation, wall lining, and roofing. Hydraulic engineers use copper sheets for tightening on dams, sluices (floodgates), and bridges.

Other areas of application are in the fabrication of household articles, art objects, coins and medals, and in military hardware as ammunition. There is a smaller demand for other purposes, such as electrodeposition; powder-metallurgical copper, special materials for brakes and self-lubricating bearings, small precision parts, filters, graphite brushes; and alloying additives for aluminum, iron, and steel. Use in copper compounds, chiefly copper sulfate and copper oxides, consumes only 1–2% of the primary world production.

Table 8.20 lists the distribution of copper consumption among various industries. This

distribution is effectively determined by the specific useful properties of copper. The use of copper (including alloys) in the United States in 1982, based on essential properties, can be broken down as follows [201]:

Electrical conductivity	57.0%
Corrosion resistance	21.9%
Thermal conductivity	12.1%
Constructional behavior	7.4%
Aesthetic effects	1.6%

Table 8.20: Industrial use of copper (including alloys) in the Western world in 1981, percentage by country [200].

Branch	United States	United Kingdom	Germany	Japan
Electrical and electronic industry	46	55	52	52
Industrial machinery and equipment	19	12	14	15
Building construction	16	11	15	9
Transportation	10	13	11	17
Other	9	9	8	7

Substitution and Miniaturization. Several materials compete with copper and may substitute for it, depending on the relative costs. Copper is partly replaced by aluminum in automotive radiators and in transmission cables, high-voltage long-distance lines, and household wiring. Copper wires and cables for telecommunications are being displaced by microwave technology and fiber optics. Copper is being replaced by plastics for water pipes in both residential and commercial construction. In the area of corrosion-resistant materials, in addition to plastics there are also stainless steel and titanium.

The movement toward making smaller and smaller parts has been one of the most pervasive and continuing pressures on the copper market. A dramatic drop in the use of copper has occurred in the widespread acceptance of printed circuits. The use of wire has plummeted. The number and size of the connectors have dropped. On the other hand, miniaturization has steadily decreased the cost of the final products, thus increasing the number of units sold.

The average cross section of parts has steadily decreased. At one time, 0.813 mm was a base point for metal thickness, but this has decreased generally to 0.250 mm and in

electronics even to 0.250 mm. In electronics, formerly 4500 kg of metal was necessary to furnish products to a consumer market that currently requires less than 900 kg.

Table 8.21: Mine production of copper [202].

Country or region	Copper content ($\times 10^3$ t)			Percentage (1983)
	1973	1978	1983 ^a	
Chile	735	1034	1257	15.3
United States	1559	1358	1038	12.6
Canada	824	659	625	7.6
Zambia	707	643	543	6.6
Zaire	489	424	502	6.1
Peru	208	376	322	3.9
Others	1516	1605	1924	23.4
Western world	6038	6099	6211	75.5
Eastern countries	1473	1754	2009	24.5
World total	7511	7853	8220	100

^a The 1983 mine production is given for more countries and regions in Table 8.22.

At the same time, however, this drive towards miniaturization, whether in the thickness of an automotive radiator or in the size of an electronic component, is a challenge to the copper industry to produce purer copper and more useful alloys and to the copper fabricating industry to produce the new miniaturized products.

8.8 Economic Aspects

There are numerous tabular compilations of statistics on copper resources, production, and consumption [202–206]. Many books deal with economic relations and commercial problems, e.g., [207–210]. Compilations of companies in the nonferrous metal industry [211] and the mining industry [212] are published at irregular intervals.

Production and Consumption. The copper production of mines, smelters, and refineries and the consumption by country and region are given in Tables 8.21 and 8.22. Production and consumption per capita are listed in Table 8.23. Over the decades, the annual per capita consumption of primary copper in the United States has grown [205]:

Late twenties	7.5 kg
Early thirties	2.5 kg
World War II	9.5 kg
Postwar period	7.5 kg
1970	13.3 kg
1979	14.6 kg

During the 1980s, there has been no increase in consumption in America and Europe and only a small increase worldwide.

Prices. The development of copper prices since 1850 is shown in Figure 8.27. The fluctuation caused by political and economic events after World War II are conspicuous.

Table 8.22: Production and consumption of copper in 1983 ($\times 10^3$ t) [202].

Country or region	Production			Consumption of refined copper
	Mine	Smelter	Refinery	
Austria			41.9	21.9
Belgium-Luxembourg		2.8	404.6	258.2
Finland	37.8	70.1	55.4	65.8
France	0.1		43.9	390.0
Germany	1.2	159.1	420.3	737.0
Italy	1.6		31.2	325.0
Norway	26.2	26.5	22.7	9.0
Portugal	2.4	2.8	4.6	12.3
Sweden	64.0	78.8	63.4	113.0
Spain	63.9	89.0	158.6	122.5
United Kingdom				
Yugoslavia	0.7		144.4	358.0
Other ^a	129.5	86.8	123.7	133.5
	2.6	2.8		53.4
Europe*	327.5	515.9	1514.7	2599.6
India	43.8	35.4	28.1	96.0
Indonesia	78.6			16.7
Iran	65.0	47.0	10.0	
Japan	46.0	944.6	1091.9	1216.3
Korea (South)	2.6	113.0	134.8	152.3
Malaysia	29.1			17.9
Oman	11.0	7.6	3.8	
Philippines	271.4	38.8	38.8	5.0
Taiwan		37.9	38.0	104.8
Turkey	24.9	18.3	31.8	57.9
Other	1.5			20.8
Asia*	573.9	1242.6	1377.2	1687.7
South Africa	211.8	192.3	157.7	73.6
Botswana	20.3			
Morocco	24.2			
Namibia	52.1	54.2		
Zaire	502.2	465.8	226.9	23.5
Zambia	542.8	562.7	575.4	
Zimbabwe	23.7	31.2	25.4	
Other	0.3		2.4	
Africa	1377.4	1306.2	987.8	97.1

Country or region	Production			Consumption of refined copper
	Mine	Smelter	Refinery	
United States	1038.1	927.7	1583.7	1775.4
Argentina				37.0
Brazil	33.0	63.1	88.5	148.4
Canada	625.0	336.9	464.3	195.0
Chile	1257.1	1058.1	833.4	23.8
Mexico	206.1	66.9	80.2	79.2
Peru	322.2	295.9	190.6	18.3
Other ^b	2.8			6.0
America[†]	3484.3	2748.6	3240.7	2283.0
Australia	264.2	173.6	201.9	114.8
New Zealand				0.4
Papua New Guinea	183.2			
Australia and Oceania	447.4	173.6	201.9	115.2
Western world	6210.5	5986.9	7322.3	6782.6
USSR	1180.0	1280.0	1500.0	1360.0
Bulgaria	80.0	60.0	62.0	62.0
Germany (DDR)	12.0	17.0	50.0	115.0
Poland	402.3	320.0	360.1	176.6
Romania	28.0	40.2	47.0	68.0
China	175.0	195.0	310.0	410.0
Korea (North)	10.0	35.0	35.0	17.0
Mongolia	95.0			
Other	27.0	22.5	47.9	124.4
Eastern countries and Cuba	2009.3	1969.7	2412.0	2333.0
Total	8219.8	7956.6	9734.3	9115.6

^a Excluding Eastern countries.

^b Excluding Cuba.

Table 8.23: Per capita production and consumption of copper, kilograms per person, in 1979 [205].

Country or region	Production	Consumption
United States	9.0	14.6
Japan	8.5	15.1
Germany	6.2	16.5
Economic Community (EEC)	3.6	11.6
Western world	2.4	3.4
USSR	5.6	—
World	2.2	—

Prices are set primarily at two metal exchanges: the London Metal Exchange (LME) and the New York Commodity Exchange (Comex).

Product Promotion. Two international organizations deal with copper promotion, re-

search, and development: the Conseil international pour le développement du cuivre (CIDEC) and the International Copper Research Association (INCRA).

Three European Institutions are the Deutsches Kupfer-Institut e.V. (DKI), Berlin; the Copper Development Association (CDA), London; and the Centre d'information cuivre, laiton et alliages, Paris.

In 1968, four developing countries that are among the main copper ore exporters in the world—Chile, Peru, Zambia, and Zaire—formed an association, CIPEC (Conseil intergouvernemental des pays exportateurs de cuivre). Some other countries have since joined.

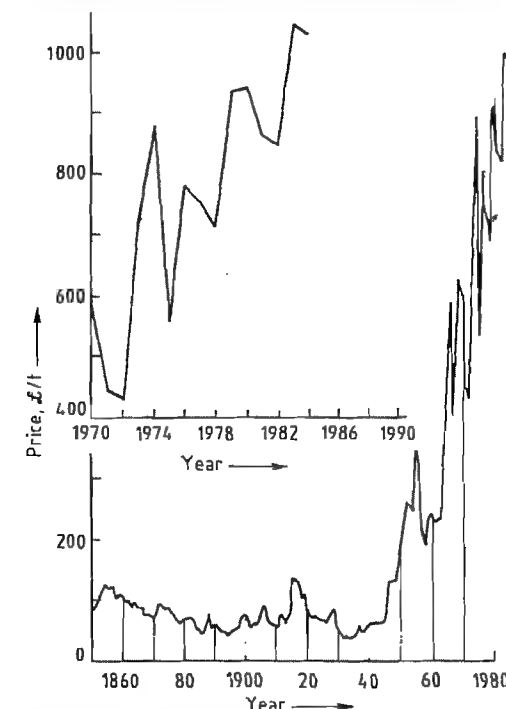


Figure 8.27: Annual average copper prices in London between 1850 and 1984 [202].

8.9 Environmental Protection

The worldwide growth of industry and population has caused a series of environmental problems, particularly the following: (1) emis-

sion control; (2) water protection; (3) solid-waste disposal.

Emission Control. There are two important tasks in the treatment of off-gas from pyrometallurgical processes in copper metallurgy: the removal of sulfur dioxide and the containment of flue dust.

Because most copper comes from sulfide ores, sulfur is the main problem in copper extraction. In pyrometallurgical operations, it appears as sulfur dioxide (Table 8.24) [214–215]. The mass ratio of sulfur to copper in sulfidic concentrates is usually between 0.8 and 1.6. Consequently, a large quantity of sulfur dioxide must be captured because of its harmful effects on health, vegetation, and property. In most cases, sulfuric acid is produced from the SO_2 -containing off-gas [216].

Flue dust can be separated from off-gas to a high degree in modern gas-cleaning systems such as electrostatic precipitators, baghouses, cyclones, and wet scrubbers. This metal-containing dust is recycled.

A growing problem is caused by the increasing arsenic content of available copper ores—the so-called dirty copper ores. Much of the arsenic is removed as arsenic trioxide during pyrometallurgical operations by volatilization and can be captured with flue dust [217].

Table 8.24: Comparison of SO_2 concentrations in copper smelting off-gas [213].

Process	SO_2 , vol %
Multiple-hearth roasting	5–8
Fluidized-bed roasting	8–15
Sinter roasting	1–2
Blast furnace smelting	2–5
Reverberatory furnace smelting	0.5–2.5
Electric furnace smelting	0.5–5
Outokumpu flash smelting	10–30
INCO flash smelting	75–80
KIVCET process	80–85
Peirce-Smith converter	5–12
Hoboken converter	7–17
TBRC process	1–15
Mitsubishi process	15–20
Noranda process	10–20

Water Protection. Harmful wastewater does not usually result from pyrometallurgical copper production but water for direct or indirect cooling of furnaces, casting machines, and

cast copper products is required on a large scale. This cooling water is moderately warmed, but does not acquire chemical impurities. Closed circulation is used as much as possible in modern plants.

Hydrometallurgical operations for the extraction of copper from ores or concentrates present the risk of water pollution. These solutions, of various compositions, must be post-treated if they cannot be recycled. Such post-treatment consists of neutralization or precipitation of specific ions, chiefly anions bearing sulfur and the cations of heavy metals. Lime is an excellent precipitant. Thus, the sulfate ion in sulfuric acid solutions formed during hydrometallurgical extraction is precipitated as gypsum [218].

Solid-Waste Disposal. The following means are used for handling solid residues:

- Recycling
 - Exploitation as raw material for the preparation of useful products
 - Dumping in deposits
- One example of each method follows:
- Flue dust from pyrometallurgical operations, e.g., from the Outokumpu flash smelting process, are added to the feed and recycled into suitable furnaces and occasionally into blast furnaces after agglomeration. Zinc-containing flue dusts can be processed into zinc and zinc compounds.
 - Discarded slags with low copper content from some copper smelting processes can be sold after suitable treatment.
 - Hydrometallurgical techniques yield various precipitates such as elemental sulfur or impure gypsum, which can easily be deposited.

8.10 Toxicology

Copper is a vital trace element for humans, most animals, and plants. For higher organisms, the compact metal is completely harmless. However protista, especially bacteria, die in contact with metallic surfaces of copper and

many of its alloys (oligodynamic effect) [219–220].

Continued exposure to the metal dust or fumes can irritate mucuous membranes. The following exposure limits have been established:

Form	Germany	United States
Metal dust	MAK 1 mg/m ³	TLV/STEL 2 mg/m ³
Metal fumes	MAK 0.1 mg/m ³	TLV/TWA 0.2 mg/m ³

8.11 Compounds

Copper compounds, although they represent a small fraction of total copper production, play an important and varied role in industry and agriculture. One of the oldest known fungicides was copper-based and was used extensively in the early part of the century. The last 20 years have brought about a resurgence in the use of copper-based fungicides partly because of a lack of tolerance by fungi to copper and also because of its relatively low toxicity to higher plants and animals. Although copper is an essential trace element for higher plants and animals, it is acutely toxic in higher doses. Copper compounds are used as nutritional additives in animal feeds and fertilizers, and are found in a variety of dietary supplements. Copper salts are used in the control of algae in lakes and ponds, and the oxides are used in antifouling paints and coatings. Copper acetoarsenite, Paris green, is used as an insecticide, and copper chromium arsenate is an effective alternative to creosote for the preservation of wood.

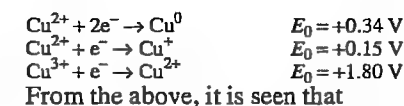
Copper and its compounds are used catalytically in numerous organic reactions, e.g., polymerization, isomerization, and cracking reactions. They are used in the textile and dye industries in the preparation of rayon and acrylonitrile, as mordants and oxidants in textile dyeing and printing, and in the preparation of azo dyes. Copper compounds are used as pigments in glass, ceramics, porcelains, varnishes, and artificial gems, and in the manufacture of the copper phthalocyanine pigments. Copper salt solutions are used for

electroplating, in brazing and burnishing preparations, and as brighteners for aluminum. Solutions of copper(I) complexes are used to selectively absorb carbon monoxide, butadiene, and alkenes from gas streams. In the petroleum industry, copper compounds are used as deodorizing (desulfurization) and purifying agents. Copper(II) carbonate is used in drilling muds to protect against release of poisonous hydrogen sulfide gas, and copper(I) iodide is used in acid muds to bind corrosion inhibitors to the iron drills. More recent applications of copper compounds are in pollution control and solar technology.

The multitude of applications of copper compounds in the biosphere is largely responsible for the extent of academic interest in them. Also, the facile reduction–oxidation of the copper(I)–copper(II) couple, the ease of theoretical treatment of the d^9 copper(II) system, and the varied stereochemistries and magnetic behaviors associated with copper ions enhance their theoretical appeal. Since this treatment of copper compounds is primarily from an industrial perspective, the reader whose interest is academic is referred to the classic references [221–224] as well as to more recent materials [225–231] that are attune to the subtle chemistries of copper and its compounds. Compounds of primary industrial importance are distinguished from compounds of minor importance in this section.

8.11.1 The Copper Ions

Copper, $[\text{Ar}] 3d^{10} 4s^1$, is a member of the first transition series. It is classified as a transition element in the broader definition because the copper(II) valence state, $[\text{Ar}] 3d^9$, comprises such a large proportion of the defined chemistry of copper. Copper in its compounds exists primarily in two oxidation states, 1+ and 2+. Although copper(0) and copper(III) compounds have been identified, they are not presently of commercial importance. The stabilities of the various valence states of copper are illustrated by the following standard reduction potentials:



From the above, it is seen that



with $pK = -5.95$

In other words, the free copper(I) ion does not exist to any appreciable extent in aqueous solution. In the presence of ligands such as ammonia, chloride, or cyanide, solutions of copper(I) can be prepared that are stable with respect to disproportionation. For example, the colorless solution of tetraamminedicopper(I) sulfate is prepared readily by contact of blue tetraamminecopper(II) sulfate with metallic copper in the absence of air. Upon acidification with sulfuric acid, copper powder and a copper(II) ammonium sulfate solution are produced. The insoluble copper(I) chloride can be produced by sulfuric acid acidification of a copper(I) ammine chloride solution. If the solution is acidified with hydrochloric acid, a solution of $[\text{CuCl}_2]^-$, $[\text{CuCl}_3]^{2-}$, or $[\text{CuCl}_4]^{3-}$ species is produced, depending on chloride concentration. Copper(I) chloride is stable to water because of its insolubility, which is a result of the polymeric structure that arises from the chloride's ability to bridge copper. This contrasts with the sulfate's inability to coordinate or bridge strongly. Consequently, copper(I) sulfate can be produced only in nonaqueous media.

The electronic structure of the copper(I) ion is $[\text{Ar}] 3d^{10}$. The compounds are diamagnetic and colorless except where charge-transfer bands arise. Copper(I) is isoelectronic with zinc(II) and the preferred stereochemistries are similar. As a result of the filled 3d level, no ligand field stabilization occurs and electronic distortions are minimized. The stereochemistry around the copper(I) ion is determined mainly by the size of the anions, as well as by the electrostatic and covalent bonding forces. The preferred stereochemistry is tetrahedral, with linear and trigonal planar compounds also being common.

The majority of copper(II) compounds exhibit square planar or distorted octahedral configurations about the copper ion. The $3d^9$

electronic structure gives rise to the classic example of Jahn–Teller distortion in which the four planar metal–ligand distances are smaller than the two axial distances. Copper(II) ions are also found in distorted tetrahedral and various five-coordinate environments.

The copper(II) ion, $[\text{Ar}] 3d^9$, is predominantly blue or green, and the unpaired $3d$ electron results in magnetic phenomena. In most copper compounds, the unpaired electrons of the copper ions are sufficiently isolated from each other so that the compounds exhibit paramagnetic behavior. However, there are many polynuclear copper compounds in which the spins are coupled, which lowers the magnetic moment. The coupling may be so weak that it must be observed near the absolute zero of temperature, or it may be strong enough to render the compound diamagnetic at room temperature or above.

8.11.2 Basic Copper Compounds

8.11.2.1 Copper(I) Oxide

Cu_2O , m_p 1235 °C, d_4^{25} 5.8–6.2, decomposes above 1800 °C. It occurs in nature as the red or reddish brown mineral cuprite with a cubic or octahedral crystal morphology. Depending on the method of preparation and particle size, the synthetic material is yellow, orange, red, or purple. The yellow material has erroneously been referred to as copper(I) hydroxide, but X-ray diffraction patterns indicate that there are no differences in the crystal structures of the colored forms. Their thermodynamic data are as follows: c_p (298 K) 429.8 $\text{J kg}^{-1}\text{K}^{-1}$, c_p (290–814 K) 519.2 $\text{J kg}^{-1}\text{K}^{-1}$, c_p (290–1223 K) 565.2 $\text{J kg}^{-1}\text{K}^{-1}$, ΔH^0 (25 °C) –166.6 kJ/mol. Copper(I) oxide is stable in dry air but slowly oxidizes to copper(II) oxide in moist air. It is practically insoluble in water but dissolves in aqueous ammonia. In excess hydrochloric acid, soluble copper(I) chloride complexes are formed; however, in dilute sulfuric or nitric acids, disproportionation to the soluble copper(II) salts and copper powder results.

Production. Copper(I) oxide is produced easily by a variety of methods; its instability with respect to oxidation requires careful consideration. Copper(I) oxide produced pyrometallurgically is usually coated with isophthalic acid or pine oil to preserve its integrity [232]. Hydrometallurgically produced material can be stabilized by mixing the particle slurry with glue, gelatin, casein, or dextrin before drying [233–236].

Pyrometallurgical Processes. Copper(I) oxide is formed when copper powder is heated above 1030 °C in air; to prevent further oxidation, it must be cooled quickly in an inert atmosphere. To allow for lower temperature production of copper(I) oxide, carbon can be blended with copper(II) oxide and heated to 750 °C in an inert atmosphere. The material must be stabilized by coating the formed particles with isophthalic acid or pine oil [232]. A more stable copper(I) oxide results when stoichiometric amounts of copper powder and copper(II) oxide are blended, heated to 800–900 °C in an inert atmosphere, and allowed to cool. The production can be effected at lower temperature if ammonia or certain ammonium salts are added to the blend [237–239]. The autoclave oxidation of copper metal at 120 °C and about 0.6 MPa gauge pressure with air in the presence of water and small amounts of sulfuric and hydrochloric acids produces a red, pigment-grade product [240]. By varying the pressure and temperature, considerable differences in particle size, coloring, apparent bulk density, and buoyancy have been found.

Hydrometallurgical Processes. Tetraamminedicopper(I) sulfate, $\text{Cu}_2(\text{NH}_3)_4\text{SO}_4$, prepared by leaching an excess of copper with a solution of ammonia and ammonium sulfate, with air as the oxidant, yields a red copper(I) oxide upon acidification to pH 3–5 [241]. The less corrosive ammonium carbonate leach system in which $\text{Cu}_2(\text{NH}_3)_4\text{CO}_3$ is produced is more common. Upon vacuum distillation, a very stable red Cu_2O product remains [241]. If sodium hydroxide is added to the leach liquor, a yellow microcrystalline powder is precipitated [242]. When the yellow Cu_2O is heated in an excess of sodium hydroxide, it is con-

verted to an orange material of somewhat larger particle size.

Steam stripping of the copper(I) ammine carbonate solution yields a brown, impure product [243] which can be converted to a red material by washing it in an organic acid, e.g., formic or acetic acid [244]. An impure, brown product can also be converted to a red material by boiling it in 20% sodium hydroxide solution [245].

If a saturated solution of copper(I) ammine carbonate is agitated over copper metal, a layer of red copper(I) oxide is continuously produced which can be broken loose and recovered [246]. When copper salts are leached with chelating agents such as ethylenediaminetetraacetic acid [247] or ammonia [248] under pressure of carbon monoxide or hydrogen, and sodium hydroxide is subsequently added, a relatively stable, yellow copper(I) oxide is obtained; the reaction is catalyzed by an alkali metal iodide [249].

The reduction of a boiling slurry of basic copper(II) sulfate with sulfur dioxide at a pH of about 3 produces a reddish product [250]. Red copper(I) oxide has also been prepared by mixing a slurry of basic copper(II) sulfate with neutral copper(II) sulfate and adding sodium sulfite to a pH of 5.2. The mixture is then acidified to pH 3.5–5 and heated to boiling. The intermediate copper(I) sulfite slurry is decomposed to copper(I) oxide and sulfurous acid. Alkali is subsequently added to maintain a pH of 2.6–2.8 [251].

When a solution of copper(I) chloride and sodium chloride is neutralized with sodium hydroxide and then heated to 138 °C under pressure, a red copper(I) oxide is obtained which has an average particle diameter of about 2.5 μm [252]; an orange product (about 1- μm particles) is prepared by neutralizing the solution to pH 8.5 at 60 °C [253]. Simultaneous mixing of copper(I) chloride solutions with sodium chloride and sodium hydroxide solution in the presence of copper(I) oxide seed crystals at a controlled pH of 10.0, 55 °C, and under nitrogen, gives a reddish purple material (average diameter 48 μm). At pH 7.0, a

yellow material is obtained with an average particle size of 0.4 μm [254].

The electrolytic production of copper(I) oxide between copper electrodes in brine yields a yellow product at room temperature. At higher temperature, an orange or red material is produced.

Uses. The largest commercial use of copper(I) oxide is in antifouling paints for boat and ship bottoms; it is an effective control for barnacles and algae. The yellow or orange copper(I) oxide is used as a seed and crop fungicide, and the red material is used as a pigment in ceramic glazes and glass. Copper(I) oxide is also used in rectifiers and in brazing. Numerous organic reactions are catalyzed by copper(I) oxide, and it is an effective absorbent for carbon monoxide.

Analysis and Specifications. The ASTM approved analysis and specification for pigment-grade copper(I) oxide [255] and the military specification for the pigment grade [256] are listed in Table 8.25.

Table 8.25: Specifications for pigment-grade copper(I) oxide (%).

Assay	Navy I [256, 257]	Navy II [256]
Copper(I) oxide	97.0	90.0
Total copper (min.)	86.0	80.0
Reducing power (min.)	97.0	90.0
Nitric acid-insolubles (max.)	0.3	0.3
Chloride (max.)	0.4	0.4
Sulfate (max.)	0.1	0.1
Zinc oxide (max.)	—	10.0
Other metals (max.)	0.5	0.5
Acetone-soluble material (max.)	0.5	0.5

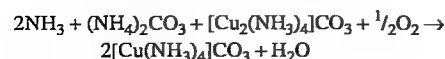
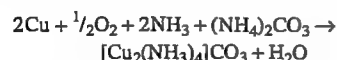
8.11.2.2 Copper(II) Oxide

CuO , m_p 1330 °C, d_4^{25} 6.48, occurs in nature as the black minerals tenorite (triclinic crystals) and paramelaconite (tetrahedral, cubic crystals). Commercially produced copper(II) oxide is usually black, although a brown product (particle size < 10^{–6} m) can also be produced. Thermodynamic data: c_p (298 K) 531.1 $\text{J kg}^{-1}\text{K}^{-1}$, c_p (290–1253 K) 682.4 $\text{J kg}^{-1}\text{K}^{-1}$, ΔH^0 (25 °C) –155.3 kJ/mol. Copper(II) oxide is stable to air and moisture at room temperature. It is virtually insoluble in

water or alcohols. Copper(II) oxide dissolves slowly in ammonia solution but quickly in ammonium carbonate solution; it is dissolved by alkali metal cyanides and by strong acid solutions. Hot formic acid and boiling acetic acid solutions readily dissolve the oxide. Copper(II) oxide is decomposed to copper(I) oxide and oxygen at 1030 °C and atmospheric pressure; the reduction can proceed at lower temperature in a vacuum. Hydrogen and carbon monoxide reduce copper(II) oxide to the metal at 250 °C and to copper(I) oxide at about 150 °C. Ammonia gas reduces copper(II) oxide to copper metal and copper(I) oxide at 425–700 °C [237].

Production. Copper(II) oxide can be prepared pyrometallurgically by heating copper metal above 300 °C in air; preferably, 800 °C is employed. Molten copper is oxidized to copper(II) oxide when sprayed into an oxygen-containing gas [257]. Ignition of copper(II) nitrate trihydrate at about 100–200 °C produces a black oxide. Basic copper(II) carbonate, when heated above 250 °C, produces a black oxide if a dense carbonate is employed; a brown material is produced when the light and fluffy carbonate is used. An alkali-free oxide can be prepared by ignition of copper(II) carbonate produced from ammonium carbonate and a copper(II) salt solution. Copper(II) hydroxide, when heated above 100 °C, is converted to the oxide.

Hydrometallurgy is the most common method for the production of copper(II) oxide. A solution of ammonia and ammonium carbonate in the presence of air effectively leaches metallic copper; the process is represented by the following reactions:



The second and third reactions proceed readily; the first is slow. Consequently, in batch operations the leach is usually begun with a small charge of the copper solution, but

continuous operations offer significantly improved rates. The leach liquor is then filtered to remove iron impurities and metallic copper, and is subsequently oxidized by air sparging. If necessary, lead and tin are removed by treatment with strontium, barium, or calcium salts [258–261]. The solution is filtered again and stripped of ammonia and carbon dioxide by steam injection or pressurized boiling to produce a black copper(II) oxide [258]. The ammonia and carbon dioxide are recycled for further use. The process is illustrated in Figure 8.28. Alternatively, the leach liquor can be treated with strong alkali to precipitate the intermediate copper(II) hydroxide, and then boiled to remove ammonia, with subsequent decomposition of the hydroxide to the black oxide.

Flue dust can be separated from off-gas to a high degree in modern gas-cleaning systems such as electrostatic precipitators, baghouses, cyclones, and wet scrubbers. This metal-containing dust is recycled.

A growing problem is caused by the increasing arsenic content of available copper ores—the so-called dirty copper ores. Much of the arsenic is removed as arsenic trioxide during pyrometallurgical operations by volatilization and can be captured with flue dust [217].

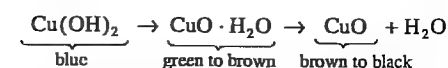
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8.11.2.3 Copper(II) Hydroxide

$\text{Cu}(\text{OH})_2$, d_4^{25} 3.37, ΔH^0 (25 °C) 446.7 kJ/mol, decomposes over 100 °C or over 50 °C in the presence of an excess of alkali. Copper(II) hydroxide is virtually insoluble in water (0.003 mg/L), and decomposes in hot

water to the more stable copper(II) oxide and water:



Copper(II) hydroxide is readily soluble in mineral acids and ammonia solution. When freshly precipitated, it is soluble in concentrated alkali, with the formation of $[\text{Cu}(\text{OH})_3]^-$ or $[\text{Cu}(\text{OH})_4]^{2-}$. Copper(II) hydroxide is inherently unstable but can be kinetically stabilized by a suitable production method.

Production. There are two classes of copper(II) hydroxide. The first is stoichiometrically rather precise, with a copper content as high as 64%; the theoretical copper content of $\text{Cu}(\text{OH})_2$ is 65.14%. This class is produced by the ammonia process [272–275], which yields a pure product of relatively good stability and large particle size. The best product results from the addition of strong alkali to the soluble copper(II) ammine complex [272, 275]. A relatively large particle-size product, deep blue in color and high in copper content, is precipitated below 35 °C. The resulting material is fairly stable or can be coated with gelatin to enhance its stability [276].

In the copper(II) hydroxide made by the ammonia process, the solubility of the copper(II) ammine complexes provides for crys-

tallite growth. This affords a large particle size, a limited surface area (point of dehydration), and hence a relatively stable product, in contrast with the unstable product (valuable assay) that results from the addition of hydroxide solutions to copper(II) salt solutions at 20 °C or above. The reaction with hydroxide is diffusion-controlled, allowing essentially no time for crystallite growth. The product is obtained as a gelatinous, voluminous precipitate with a large surface area, which is quite unstable and difficult to wash free of impurities. If the same reaction, with the same order of addition, is allowed to occur at 0–10 °C, a product of defined particle size and measurable surface area results, with greater stability but low assay.

The second class of copper(II) hydroxide, which represents a “stable” product but has lower assay and greater impurity, is produced from an insoluble precursor such as basic copper(II) carbonate or copper(II) phosphate. The first stable copper(II) hydroxide of this kind was made from copper(II) phosphate with alternate additions of copper(II) sulfate and sodium hydroxide solutions [277]. The process is illustrated by the following series of reactions:

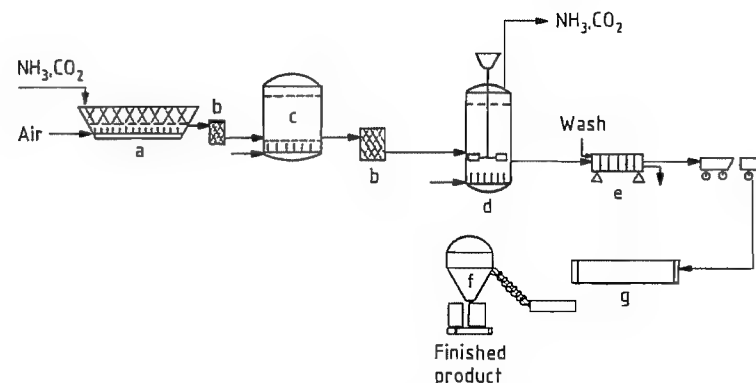
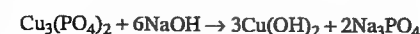
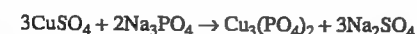


Figure 8.28: Process flow diagram for production of copper(II) oxide from ammonia–ammonium carbonate leach: a) Leach vat; b) Filter; c) Treatment tank; d) Strip tank; e) Press; f) Bag house; g) Drying kiln.

The alternate copper(II) sulfate sodium hydroxide addition is continued through 15 or 20 cycles and yields a stable product with 58–59% copper and 3–5% phosphate. The product has a small particle size and a high surface area, and is used as an agricultural fungicide.

Other stable copper(II) hydroxides of high surface area and fine particle size have been produced more recently [278–280]; the processes include the use of a copper(II) oxychloride precursor in the presence of an anionic surfactant [279] or a magnesium sulfate-precipitated precursor [278]. An electrolytically produced material has also been made by using trisodium phosphate as the electrolyte [281].

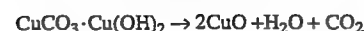
The classic Bordeaux slurry of copper(II) sulfate and lime in water has been replaced by a powdered stabilized product. This is obtained by mixing copper(II) nitrate solution and lime, adding cellulose pitch liquor (a waste product of the paper industry), and drying to yield a powder which is effective as a fungicide [282]. Sodium carbonate can be used as the precipitating agent instead of lime [283].

Uses. Copper(II) hydroxide is used as an active precursor in the production of copper(II) compounds. Ammonia-processed copper(II) hydroxide is used in the production of copper(II) naphthenate, copper(II) 2-ethylhexanoate, and copper soaps. Ammonia-processed copper(II) hydroxide is also used in the production of rayon (Schweitzer's reagent) and in the stabilization of nylon. Copper(II) hydroxides of the second class are often used as fungicides because of their small particle size. Copper(II) hydroxide is also used as a feed additive, a catalyst in the vulcanization of polysulfide rubber, and an antifouling pigment.

Analysis and Specifications. Copper is determined iodometrically with sodium thiosulfate [271]. The analysis of typical ammonia-processed copper(II) hydroxide (mass fractions in %) is copper 63.0, iron 0.05, zinc 0.05, lead 0.05, naphthenic acid-insoluble material 2.0, sulfate 0.3.

8.11.2.4 Copper(II) Carbonate Hydroxide

Copper(II) carbonate hydroxide, also called basic copper(II) carbonate, occurs in nature as the metastable mineral *azurite*, also called *chessylite*, a blue, monoclinic crystalline or amorphous powder with a formula approximating $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, d_4^{24} 3.8, ΔH^0 (20 °C) -87.4 kJ/mol, and *malachite*, green, monoclinic crystals with a formula approximating $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, d_4^{25} 3.9–4.0, ΔH^0 (20 °C) -57.7 kJ/mol. The copper(II) carbonate of commerce, malachite, is also known as Bremen green. Pure copper(II) carbonate, CuCO_3 , has not been isolated. Copper(II) carbonate is virtually insoluble in water but dissolves readily in aqueous ammonia and alkali metal cyanide solutions. Copper(II) carbonate dissolves quickly in mineral acid solutions and warm acetic acid solution, with the formation of the corresponding copper(II) salt. Malachite is much more stable than copper(II) hydroxide but slowly decomposes to the oxide according to the following reaction:



Malachite is rapidly decomposed to the oxide above 200 °C.

Production. Two grades of copper(II) carbonate are available commercially, the light and the dense. The light grade is a fluffy product of high surface area. It is precipitated by adding a copper(II) salt solution, usually copper(II) sulfate solution, to a concentrated solution of sodium carbonate at 45–65 °C. Azurite is formed initially, and complete conversion to malachite usually occurs within two hours. The conversion is accelerated by the addition of malachite nuclei to the reactor.

A dark green, dense product results when a copper(II) salt solution is added to a solution of sodium hydrogen carbonate at 45–65 °C; conversion to malachite requires about one hour in this case. The density is maximized if the reactor is washed with acid prior to the precipitation to prevent premature nucleation on malachite nuclei. (A less dense product would be produced if malachite nuclei are

added to the slurry of azurite.) Solutions of copper(II) salt and sodium carbonate can also be added simultaneously at a pH of 6.5–7.0 and a temperature between 45 and 65 °C; conversion to malachite is usually complete within one hour. When a solution of copper(II) ammonium carbonate is boiled, ammonia and carbon dioxide are expelled from the solution, and a deep green, dense copper(II) carbonate precipitates [258].

Uses. Copper(II) carbonate is used as a precursor in the production of copper salts and soaps. It is used in animal feeds as a source of copper, in the sweetening of petroleum, and in electroplating for the control of pH. Copper(II) carbonate is used as a hydrogenation catalyst and as an accelerator in polymerization reactions. The light grade is somewhat effective as a fungicide and is used as a seed protectant.

Analysis and Specifications. Copper is analyzed by iodometric titration with sodium thiosulfate solution [271]. Table 8.26 gives typical analyses of light and dense technical-grade copper(II) carbonates.

Table 8.26: Typical analysis of commercially available copper(II) carbonate hydroxides.

Assay	Light, %	Dense, %
Copper	55.5	55.0
Sulfate	0.6	0.6
Iron	0.1	0.1
Zinc	0.01	0.02
Lead	0.003	0.005
Hydrochloric acid-insoluble material	0.05	0.05
Water	1.0	2.0

8.11.3 Salts and Basic Salts

8.11.3.1 Copper(I) Chloride

Copper(I) chloride, CuCl , mp 422 °C, bp 1367 °C, d_4^{25} 4.14, ΔH^0 (25 °C) -134.6 kJ/mol, occurs in nature as the colorless or gray cubic-crystal *nantokite*. The commercially available product is white to gray to green and of variable purity. Copper(I) chloride is fairly stable in air or light if the relative humidity is less than about 50%. In the presence of moisture and air, the product is oxi-

dized and hydrolyzed to a green product that approaches copper(II) oxychloride, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$. In the presence of light and moisture, a brown or blue product is obtained. Copper(I) chloride is slightly soluble to insoluble in water, with values from 0.001 to 0.1 g/L being reported. It is readily hydrolyzed to copper(I) oxide by hot water. Copper(I) chloride is insoluble in dilute sulfuric and nitric acids, ketones, alcohols, and ethers, but it quickly dissolves in hydrochloric acid, alkali halide, or ammonia solutions with the formation of complex compounds that are readily oxidized by air. Copper(I) chloride is soluble in solutions of alkali metal cyanides or thiosulfates and of coordinating amines, pyridines, and nitriles, notably, acetonitrile [284]. The increase in solubility of copper(I) chloride with chloride ion concentration illustrated in Figure 8.29 [285]. When the chloride concentration is decreased by dilution with water, the pure white copper(I) chloride precipitates.

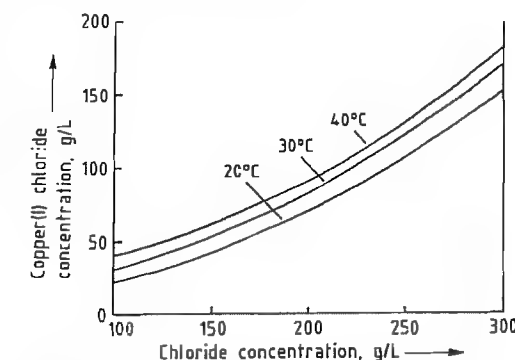
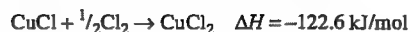
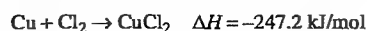


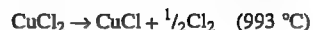
Figure 8.29: Solubility of copper(I) chloride in excess chloride ion solution at different temperatures.

Production. The direct combination of the elements is the most common method of production. The reaction of copper metal and chlorine is not spontaneous at ambient temperature. Once the metal is heated to red heat in the presence of chlorine, the reaction is self-sustaining and requires external cooling to prevent the metal from melting. A number of similar patents exist [286–289] in which copper metal is reacted with chlorine gas to produce a molten copper(I) chloride that is cast and pulverized. The primary difference in con-

ditions is the use of a shaft furnace [286] as opposed to the use of crucibles. The recommended process temperature varies from 450 to 800 °C [286, 287] or 500 to 700 °C [288, 289]. The conditions required for the high-temperature production of a pure copper(I) chloride can be illustrated by the following:



Higher temperature and excessive contact with copper metal favor the production of a very pure copper(I) chloride. The lowest possible temperature is obviously 422 °C, the melting point of copper(I) chloride. As the temperature approaches the decomposition temperature for the reaction



a product of higher purity is obtained. Operationally, a temperature between 750 and 900 °C is ideal, and results in a product of > 98% purity. The process of Degussa [287] illustrates a commonly used commercial process for the high-temperature production of copper(I) chloride; Figure 8.30 shows a suitable crucible for the production of technical-grade copper(I) chloride. Once the reaction is initiated, chlorine and copper metal (shot, chopped wire, or briquettes) are added continuously. As the molten product is formed on the surface of the upper metal layer, it flows by gravity down through the porous copper bed to effect further reduction of any copper(II) chloride, and out the exit port onto a rotating table where the product is allowed to cool and solidify. The flakes that form are packaged as is or ground to a powder and packaged. Because of the high temperature during the reaction and the volatility of copper(I) chloride, the exit port must be vented to a caustic scrubber. When the molten product is allowed to fall onto a high-speed, horizontally rotating disk constructed of quartz, graphite, or porcelain, small prills of uniform size are produced [290]. The product is spun out onto a water

cooled diaphragm and collected. If the copper is contaminated with oxides, hydrogen chloride gas should be added to the chlorine gas stream to prevent the production of basic copper(II) chlorides that would contaminate the product [286].

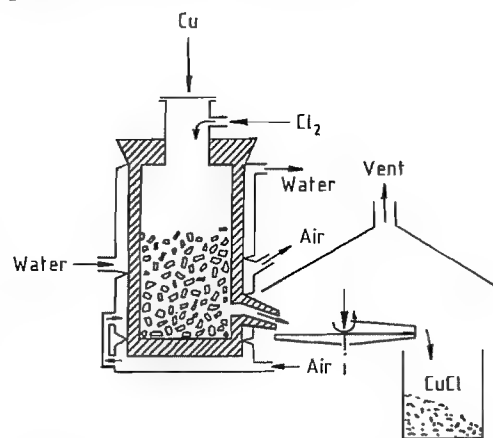


Figure 8.30: Crucible used in the production of copper(I) chloride.

If the product is packaged quickly and sealed properly, no extreme precautions are required. Otherwise, the product must be stored under nitrogen to preserve its integrity or coated with mineral oil as a barrier to moisture. Copper(I) chloride is also produced hydrometallurgically by the reduction of copper(II) in the presence of chloride ions [291]:



Other reducing agents can be used, such as metallic copper, sulfurous acid, hydroxylamine, hydrazine, or phosphorous acid. The copper(I) chloride solution is produced, for example, by mixing a copper(II) chloride solution with metallic copper in the presence of hydrochloric acid or sodium chloride. The colorless to brown solution is stable only in the absence of air. Continuous preparations of copper(I) chloride solutions have been developed [292, 293]. When they are diluted with water, a white crystalline material precipitates which can be vacuum dried or washed with sulfurous acid, then with alcohol and ether, and carefully dried. Zinc has also been used as

a reducing agent in a more recent process [294].

Production of copper(I) chloride by treatment of ores with iron(III) chloride solutions [295, 296] and recovery of the product through chlorination in pit furnaces above 800 °C [297] have also been attempted.

Uses. Copper(I) chloride is used as a precursor in the production of copper(II) oxychloride and copper(I) oxide, as well as fine copper powder [298]. The production of silicone polymers, the vulcanization of ethylene-propylene rubbers (EPDM) [299], and acrylonitrile production are other applications. Copper(I) chloride is also used in the purification of carbon monoxide gas [300–303] and the production of phthalocyanine pigments [304, 305]. More recently, copper(I) chloride has been found to be an effective catalyst in the production of dialkyl carbonates [306–308].

Analysis and Specifications. Copper(I) chloride is analyzed according to [271]. Table 8.27 lists specifications for technical- and reagent-grade material.

Table 8.27: Specifications for copper(I) chloride.

Assay	Technical-grade, %	Reagent-grade, %
Copper (min.)	97.0	90.0
Acid-insolubles (max.)	0.1	0.02
Iron (max.)	0.01	0.005
Sulfate (max.)	0.3	0.10
Arsenic (max.)	—	0.001
Not precipitated by H ₂ S as sulfate (max.)	—	0.2

8.11.3.2 Copper(II) Chloride

Copper(II) chloride, CuCl_2 . *mp* (extrapolated) 630 °C, d_4^{25} 3.39, begins to decompose to copper(I) chloride and chlorine at about 300 °C. The often reported melting point of 498 °C is actually a melt of a mixture of copper(I) chloride and copper(II) chloride. Decomposition to copper(I) chloride and chlorine is complete at 993 °C. The deliquescent monoclinic crystals are yellow to brown when pure; their thermodynamic data are as follows: c_p (298 K) $-579.2 \text{ J kg}^{-1} \text{ K}^{-1}$, c_p (288–473 K) $-621.7 \text{ J kg}^{-1} \text{ K}^{-1}$, c_p (288–773 K)

$-661.9 \text{ J kg}^{-1} \text{ K}^{-1}$, ΔH^0 (25 °C) -247.2 kJ/mol . In moist air, the dihydrate is formed. Figure 8.31 shows the solubility of copper(II) chloride in water and hydrochloric acid at two temperatures [309]. At higher concentrations of hydrogen chloride, $[\text{CuCl}_3]^-$ and $[\text{CuCl}_4]^{2-}$ complexes are formed. Copper(II) chloride is easily soluble in methanol and ethanol and moderately soluble in acetone.

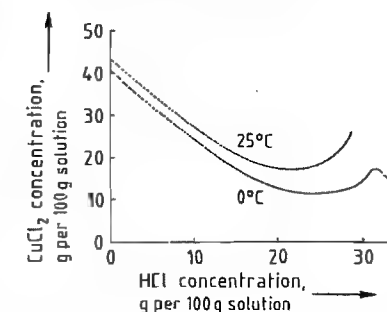


Figure 8.31: Solubility of copper(II) chloride in hydrochloric acid solutions at different temperatures.

The more common commercial form of copper(II) chloride is the dihydrate, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, *mp* around 100 °C (with decomposition to the anhydrous form). This occurs in nature as blue-green orthorhombic, bipyramidal crystals of eriochalcite, d_4^{25} 2.51. Its solubility characteristics are proportionally similar to those of the anhydrous form. In moist air the dihydrate deliquesces, and in dry air it effloresces.

Production. Because of the relative stabilities of copper(I) chloride and copper(II) chloride at high temperature, it is improbable that a pure anhydrous copper(II) chloride can be prepared by excessive chlorination of copper in a melt, even though such methods have been reported. The most common method for the production of anhydrous copper(II) chloride is by dehydration of the dihydrate at 120 °C. The product must be packaged in air-tight or desiccated containers.

The dihydrate can be prepared by the reaction of copper(II) oxide, copper(II) carbonate, or copper(II) hydroxide with hydrochloric acid and subsequent crystallization. Commercial production of copper(II) chloride dihy-

drate uses a tower packed with copper. An aqueous solution is circulated through the tower. Sufficient chlorine is passed into the bottom of the tower to oxidize the copper completely [292, 293]; to prevent hydrolysis [precipitation of copper(II) oxychloride] of concentrated copper(II) chloride solutions, they are kept acidic with hydrochloric acid. The tower can be operated batchwise or continuously; Figure 8.32 shows the continuous operation. A hot, concentrated liquor is circulated continuously through the tower, and the overflow from the tower is passed through a crystallizer where the liquor is cooled; the product is then centrifuged, dried, and packaged. The addition of hydrogen chloride is pH controlled; the addition of water is controlled by specific gravity. Copper is added daily or twice daily, as needed.

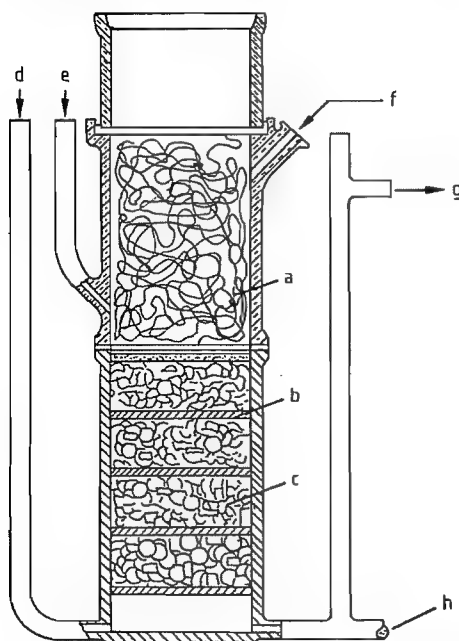


Figure 8.32: Reactor for the production of copper(II) chloride solutions: a) Copper metal; b) Porous plates; c) Raschig rings; d) Chlorine inlet; e) Steam inlet; f) Solution recycle; g) Solution to crystallizer; h) Drain.

Uses. Copper(II) chloride dihydrate is used in the preparation of copper(II) oxychloride [310, 311]. It serves as a catalyst in numerous organic chlorination reactions such as the pro-

duction of vinyl chloride [312] or 1,2-dichloroethane [313]. Copper(II) chloride dihydrate is used in the textile industry as a mordant and in the petroleum industry to sweeten sulfidic crude oil. Copper(II) chloride solutions are used for plating copper on aluminum, and in tinting baths for tin and germanium. Copper(II) chloride dihydrate is used as a pigment in glass and ceramics, as a wood preservative, and in water treatment.

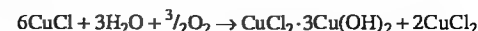
Analysis and Specifications. Copper is analyzed iodometrically with sodium thiosulfate [271]. A typical analysis of technical-grade copper(II) chloride dihydrate (in %) is as follows: copper(II) chloride dihydrate 99.0 (min.), iron 0.02, zinc 0.05, sulfate 0.05, water-insoluble material 0.01, material not precipitated by hydrogen sulfide as sulfate 0.15.

8.11.3.3 Copper(II) Oxychloride

Copper(II) oxychloride, $\text{Cu}_2\text{Cl}(\text{OH})_3$, is usually written as $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$. The trade name is copper oxychloride or basic copper chloride; the internationally accepted name (IUPAC) is dicopper chloride trihydroxide. Copper oxychloride is found in nature as the minerals paratacamite, green hexagonal crystals, and atacamite, green rhombic crystals, d_4^{25} 3.72–3.76 [314]. It is virtually insoluble in water, dissolves readily in mineral acids or warm acetic acid, and is soluble in ammonia and alkali-metal cyanide solutions. The green oxychloride is converted into blue copper(II) hydroxide in cold sodium hydroxide solution [279] and into the oxide in hot sodium hydroxide solution. With a lime suspension, copper oxychloride is converted into the blue calcium tetracuproxochloride, calcium tetracopper(II) chloride tetrahydroxide, $\text{CaCl}_2 \cdot 4\text{Cu}(\text{OH})_2$ [315]. It is decomposed to the oxide at 200 °C.

Production. Copper(II) oxychloride is most often prepared commercially by air oxidation of copper(I) chloride solutions [310, 311, 316, 317]. For this purpose, a concentrated sodium chloride solution containing about 50 g/L copper(II) is contacted with copper metal to produce a solution containing about 100 g/L

copper(I). The copper(I) chloride sodium chloride solution with or without the copper metal, is then heated to 60–90 °C and aerated to effect oxidation:

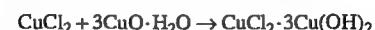
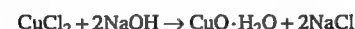


The mother liquor is separated from the precipitate and recycled into the process. The particles that are obtained by the above process are generally less than 4 µm in diameter and are suitable as crop fungicides. The particle size can be reduced further by increasing the agitation during oxidation and by utilizing a lower temperature [316]. Also, spray-drying of the product slurry gives a micronized product [318] as a result of deagglomeration of the material.

Copper(II) oxychloride can also be prepared by reaction of a copper(II) chloride solution with sodium hydroxide [314]:



or by reaction of a copper(II) chloride solution with freshly precipitated, hydrated copper(II) oxide [319]:



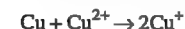
Copper oxychloride has also been produced as a by-product in the electrolytic production of copper(I) chloride [320].

Uses. Copper oxychloride is used primarily as a foliar fungicide [310, [321–325]; it is also used as a pigment.

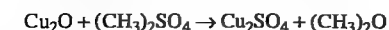
Analysis and Specifications. A typical analysis of technical-grade copper(II) oxychloride (in %) is as follows: copper 56.0, chloride 14.0 15.0, sulfate 2.0 2.5, hydroxide 22.5–23.5, water 3.0–6.0. Copper is analyzed by iodometric titration with sodium thiosulfate [271].

8.11.3.4 Copper(I) Sulfate

Cu_2SO_4 can be prepared in solution by dissolving metallic copper in a solution of CuSO_4 in absence of air:



Solid Cu_2SO_4 , however, cannot be crystallized from such solution because decomposition takes place during this operation. Solid Cu_2SO_4 can be prepared according to Recoura's method [326] by the reaction of Cu_2O with dimethyl sulfate:

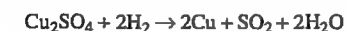


Cu_2SO_4 so prepared must be washed with ether and dried at 60 °C in a stream of argon for 24 h; it is pale beige in color. Reagent grade Cu_2O is not suitable for this purpose because it contains CuO. Freshly prepared Cu_2O from Fehling's solution is suitable. The product is about 75% pure; the remaining 25% is CuSO_4 .

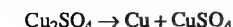
Cu_2SO_4 is also formed during the hydrogen-reduction of CuSO_4 at about 220 °C [327–332]:



However, the product will always be contaminated with unreacted CuSO_4 . If the reaction time is longer or at a higher temperature (250–300 °C), the product will be contaminated with metallic copper due to the reaction:



Cu_2SO_4 is fairly stable in dry air at room temperature but decomposes rapidly in presence of moisture:



On heating in argon, Cu_2SO_4 decomposes at about 400 °C according to:

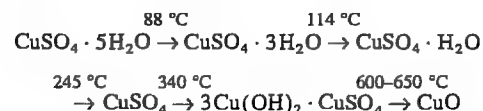


8.11.3.5 Copper(II) Sulfates

Copper(II) Sulfate Pentahydrate

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, d_4^{25} 2.285, c_p (273–291 K) 1126 J/kg⁻¹K⁻¹, ΔH^0 (25 °C) –850.8 kJ/mol, bluestone, blue vitriol, is found in nature as the mineral chalcantite, blue triclinic crystals that can be ground to a light blue powder. Copper(II) sulfate pentahydrate slowly effloresces in dry air or above 30.6 °C with the formation of the trihydrate, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. At 88–100 °C the trihydrate is produced more

quickly. Thermal analysis of the pentahydrate gives the following:

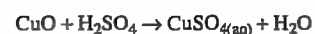


Above about 114 °C, the monohydrate is formed, and between about 245 and 340 °C, the anhydrous product CuSO_4 results. Figures 8.33A and 8.33B show solubility of CuSO_4 in water and density of the solution as a function of temperature and sulfuric acid concentration [333, 334]. The pentahydrate can be crystallized from the solution either by addition of sulfuric acid or by evaporation. Although the addition of sulfuric acid appears to be more economical, the concentration of the solution by evaporation is preferred because the crystals obtained from a "neutral" (pH 3.5–4.0) medium are less prone to hard cake formation than the acid crystals. As the particle size of the pentahydrate decreases, the tendency toward hard cake formation increases, and the necessity to increase the pH during crystallization is enforced. When a free-flowing, commercial product of fine particle size is required, such alkaline additives as calcium oxide or calcium stearate must be incorporated

into the final product to assure flowability. The incorporation of excess acid into the product accelerates the in situ dehydration of the pentahydrate and promotes hard cake formation. Lower temperature and lower humidity slow the caking process.

Copper(II) sulfate pentahydrate is soluble in methanol (15.6 g/100 mL solution) but insoluble in ethanol. It readily forms soluble alkaline complexes at sufficiently high concentrations of amines or alkali cyanides, but basic sulfates are precipitated from solution by ammonia at an intermediate pH (about 4.2–6.8). Copper(II) sulfate pentahydrate is the most commonly used copper compound because of the economics and the availability of starting materials, the ease of production, and the extent of by-product utilization (primarily copper electrowinning liquors).

Production. Copper(II) sulfate pentahydrate is prepared most easily by the reaction of a basic copper(II) compound with a sulfuric acid solution (100–200 g/L H_2SO_4), e.g.:



Copper metal, sulfuric acid, and air are the most common starting materials for the production of copper sulfate pentahydrate:

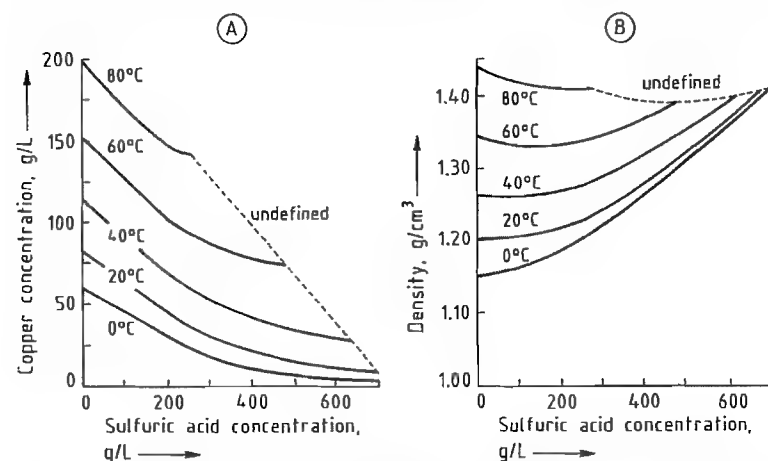
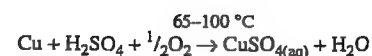


Figure 8.33: Saturated solutions of copper(II) sulfate. A) Solubility of copper(II) sulfate (as copper) as a function of sulfuric acid concentration and temperature; B) Density of copper(II) sulfate solutions as a function of sulfuric acid concentration and temperature. Reprinted with permission [334].



Harike Process. The Harike process [335] is the best commercial example of the preceding reaction (Figure 8.34). Blister shot copper up to 25 mm in diameter is added to the reaction tower (2.9 m² cross sectional area) to give a bed of copper metal 2.74-m high. Two different reaction conditions are given in Table 8.28. Condition A allows for the production of concentrated copper(II) sulfate solutions and subsequent crystallization from acid media. Condition B gives a concentrated neutral solution of copper(II) sulfate that can be crystallized or diluted with water and used for direct production of other copper products. The rate of oxygen consumption by the system is directly proportional to the mass of copper metal dissolved. Air flows of 46 m³h⁻¹m⁻² are used in order to fill with air the voids that are created by the packing of the copper shot. The solution is circulated cocurrently with the air flow to wet the particles continuously and en-

hance mixing of the solution with the copper metal. If the air flow is decreased and the voids in the copper metal bed are not filled sufficiently, the hot acid solution oxidizes the copper metal in the absence of air with the formation of a copper sulfide film. This film renders the copper metal inert to further oxidation and would lower the efficiency of the tower. On the other hand, an increase in air flow above 46 m³h⁻¹m⁻² decreases the fraction of oxygen consumed and would also result in a lowered efficiency of the tower. If an increased production (greater oxygen consumption) with good tower efficiencies is required, the height of the tower must be increased. This would also be necessary if a copper metal of lower surface area was used such as scrap copper instead of the blister shot copper. The use of cement copper and fine chopped wire creates insufficient voids for adequate air passage; such fine copper must be leached in agitated vessels.

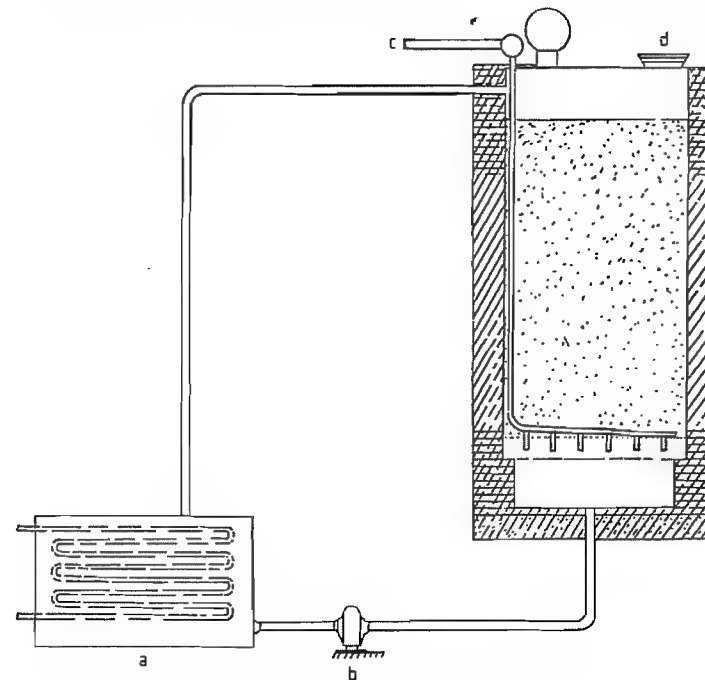


Figure 8.34: Harike tower process for production of copper(II) sulfate solutions: a) Heat exchanger; b) Circulation pump; c) Air inlet; d) Copper input.

Table 8.30: Specifications of electroless-grade copper(II) sulfate pentahydrate.

Assay	%
Copper	25.1
Iron	<0.0015
Lead	<0.003
Nickel	<0.001
Manganese	<0.0005
Chromium	<0.0005
Chlorine	nil
Water-insolubles	0.01

Anhydrous Copper Sulfate

CuSO_4 occurs in nature as the mineral hydrocyanite. It is gray to white and has a rhombic crystal morphology. It decomposes to the green basic copper(II) sulfate at 340 °C, and at 600–650 °C it decomposes to copper(II) oxide. Some of the properties of the anhydrous salt are as follows: d_4^{25} 3.6, c_p (273–291 K) 631.8 J kg⁻¹ K⁻¹, c_p (273–373 K) 657.3 J kg⁻¹ K⁻¹, ΔH^0 (25 °C) -771.6 kJ/mol. The compound is soluble in water, somewhat soluble in ethanol (1.1 g/100 mL), but insoluble in ethan-
anol. It readily dissolves in aqueous ammonia and excess alkali metal cyanides, with the formation of complexes. The material is hygroscopic, with conversion to the pentahydrate in moist air below 30 °C.

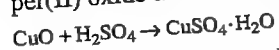
The anhydrous salt is prepared by careful heating of the pentahydrate salt to 250 °C. It can also be prepared by the reaction of hot concentrated sulfuric acid with copper metal, but purification is rather difficult.

The compound has limited commercial use but it can be used as a desiccant for removing water from organic solvents and is a sensitive indicator of the presence of moisture in such solvents.

Copper(II) Sulfate Monohydrate

$\text{CuSO}_4 \cdot \text{H}_2\text{O}$, d_4^{20} 3.25, is a whitish powder. The solubility of the monohydrate in water is identical to the pentahydrate on a copper basis. The product is hygroscopic and must be packaged in containers with moisture barriers. It is commercially produced by dehydration of the pentahydrate at 120–150 °C. A novel prepara-

tion is to triturate stoichiometric ratios of copper(II) oxide and sulfuric acid:



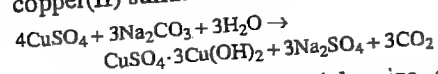
The uses of the monohydrate are analogous to those of the pentahydrate. Although there can be slight economic advantages (primarily freight costs) in using the monohydrate, market acceptance has not been great. Presently, less than 5% (copper basis) of copper(II) sulfate is marketed in the monohydrate form.

Basic Copper(II) Sulfates

Four distinct basic copper(II) sulfates can be identified by potentiometric titration of a copper(II) sulfate solution with sodium carbonate or sodium hydroxide solution [342, 343]: $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (langite), $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ (antlerite), $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ (brochantite), and $\text{CuSO}_4 \cdot \text{CuO} \cdot 2\text{Cu}(\text{OH})_2 \cdot x\text{H}_2\text{O}$. Their unique crystal morphologies are confirmed by X-ray diffraction.

The most important commercial basic copper(II) sulfate, commonly referred to as *tribasic copper sulfate*, is $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, *mp* ca. 380 °C (decomp.), d_4^{25} 3.78, occurs in nature as the green monoclinic mineral brochantite. It is readily soluble in mineral acids, acetic acid solution, and ammonia solution; it is insoluble in water. Above 650 °C it decomposes to copper(II) oxide. If anhydrous copper(II) sulfate is heated cautiously to 650 °C, another naturally occurring mineral is obtained, dolerophane, $\text{CuSO}_4 \cdot \text{CuO}$, which reacts readily with water at 20 °C to form $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ or at 100 °C to form $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ [344].

Production. Tribasic copper(II) sulfate, the commercially available basic copper(II) sulfate, is most often prepared by the addition of sodium carbonate solution to hot solutions of copper(II) sulfate:

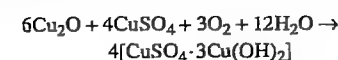
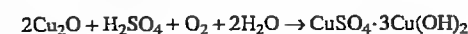


Great variation of particle size can be achieved by control of the precipitation temperature. As the temperature is increased, larger particles with greater bulk density are

formed. If a small particle size is desired, lower precipitation temperature should be used. However, as the precipitation temperature is lowered, multiple hydrates and larger amounts of sulfate are incorporated into the product; e.g., around 50 °C, the dried product contains only about 50% copper. A precipitation temperature around 90 °C is required to make a pure tribasic copper(II) sulfate.

The single largest use of the compound is as a crop fungicide, and small particles are preferred because they give a greater degree of coverage. These small particles can be obtained by high-energy attrition of the product or by carefully controlled precipitation conditions.

Another method of making tribasic copper(II) sulfate is the aeration of a suspension of copper(I) oxide in the presence of stoichiometric quantities of sulfuric acid or copper(II) sulfate [345]:



A purified, concentrated solution of copper(II) sulfate containing ammonium sulfate can be neutralized to pH 6.0–6.5 with ammonia to give a blue precipitate of approximate stoichiometry $4\text{CuSO}_4 \cdot 12\text{Cu}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. When this is dried, a green tribasic copper(II) sulfate is formed with up to 1 mol of hydration water per mole of tribasic salt [346]; the water content depends on the drying temperature.

A continuous process has been developed in which copper(II) sulfate solutions are neutralized to pH 5.9 at 30 °C by addition of gaseous ammonia to an agitated vessel [347]. A unique, germicidally active, basic copper(II) sulfate whose X-ray diffraction pattern differs from langite and brochantite has been prepared in this way [348].

Reaction of copper(II) sulfate with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and sodium hydroxide in aqueous solution gives a fine, blue, basic copper(II) sulfate powder (16% SO_4 , 2.6% PO_4 , and 54.9% Cu) that is formulated into a germicidal powder.

Tribasic copper(II) sulfate can also be prepared by cautiously heating copper(II) sulfate to 340 °C or by the aeration of a hot copper(II) sulfate solution in contact with copper metal.

Other basic copper(II) sulfates of commercial interest are the classic fungicidal mixtures, Bordeaux and Burgundy slurries, in which copper(II) sulfate solution is mixed with lime and soda ash, respectively. They are of variable stoichiometry. More recently, the aqueous Bordeaux suspension has been dried to yield a stable basic copper(II) sulfate powder of variable composition [349].

Uses. As stated earlier, basic copper(II) sulfate is primarily used as a crop fungicide [350, 351]. It has also been utilized as a precursor in the separation of copper from metallic impurities [352].

Analysis and Specifications. The analysis of a typical technical-grade tribasic copper(II) sulfate is (mass fractions in %) as follows: copper 53.5, iron 0.08, sulfate 19.0, carbonate 2.0, water 2.0–5.0. This is analyzed according to [271].

8.11.4 Compounds and Complexes of Minor Importance

8.11.4.1 Compounds

Copper(I) acetate, CuCH_3COO , is obtained as white crystals which are stable when dry but decompose on exposure to water. The product is obtained by reducing an ammoniacal solution of copper(II) acetate; on acidification with acetic acid, the crystals precipitate. Ammoniacal solutions of copper(I) acetate are used commercially to absorb olefins.

Copper(II) acetate monohydrate, neutral verdigris, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, *mp* 115 °C, d_4^{25} 1.88, decomposes at 240 °C; it forms dark green, monoclinic crystals; its solubility in water at 25 °C is 6.8 g/100 g solution; the compound is slightly soluble in methanol, diethyl ether, and acetone.

Copper(II) acetate monohydrate is produced by the reaction of copper(II) carbonate

or copper(II) hydroxide with a solution of acetic acid or by the reaction of copper(II) oxide with hot dilute acetic acid. Alternatively, the material can be made by refluxing aqueous acetic acid in the presence of copper metal and air. The technical product is generally 99% pure.

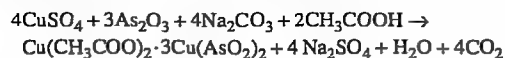
Copper(II) acetate monohydrate is used in textile dyeing and as a ceramic pigment. It is used as a fungicide, as a precursor in the production of Paris green [copper(II) acetoarsenite], and as a polymerization catalyst in organic reactions.

Basic copper(II) acetate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$ (variable), exists as blue to green salts, depending on the amount of water of hydration. Blue verdigris has the above formula, while green verdigris has fewer molecules of water of hydration. The salts are slightly soluble in water or ethanol, and soluble in dilute mineral acid or aqueous ammonia.

The basic salts are produced by neutralizing copper(II) acetate solutions. They can also be prepared by refluxing acetic acid over copper in the presence of air until the basic salt precipitates.

The basic copper(II) acetates are used as precursors in the manufacture of Paris green [copper(II) acetoarsenite] and as fungicides. They are used as pigments in oil- and water-based paints and in textile dyeing.

Copper(II) acetoarsenite, (acetato)tri-metaarsenitodicopper(II), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ (variable), also known as Paris green, is an emerald green, poisonous powder. It is virtually insoluble in water and ethanol but dissolves in dilute mineral acids and aqueous ammonia. Copper(II) acetoarsenite is primarily made by the reaction of a solution of copper(II) sulfate with arsenic(III) oxide, sodium carbonate, and acetic acid



or by the reaction of copper(II) oxide with a hot solution of acetic acid and arsenic(III) oxide. A solution of copper(II) acetate or a suspension of basic copper(II) acetate can also

react with arsenic(III) oxide. The product is used as an insecticide, in the preservation of wood, and as an antifouling pigment.

Copper(II) arsenate, $\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (variable), is a blue-green to blue insoluble powder. It is most often prepared by reaction of copper(II) sulfate solutions with arsenic(V) oxide and sodium hydroxide. Copper(II) arsenate is used as an insecticide, fungicide, rodenticide, wood preservative, and antifouling pigment.

Copper(II) arsenite, CuHAsO_3 (variable), Scheele's green, an insoluble green powder, is prepared by the reaction of a copper(II) sulfate solution with arsenic(III) oxide and sodium hydroxide and is used as pigment and insecticide.

Copper(I) bromide, CuBr , *mp* 504 °C, *bp* 1345 °C, d_4^{25} 4.72, forms white cubic crystals that slowly decompose on exposure to light or to moist air; it is soluble in hydrochloric and hydrobromic acids and in aqueous ammonia, but very slightly soluble in water. This compound is prepared pyrometallurgically [see copper(I) chloride, or by reducing a copper(II) sulfate solution in the presence of sodium bromide, usually with sulfur dioxide or metallic copper. Copper(I) bromide is used as a polymerization catalyst for organic reactions.

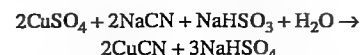
Copper(II) bromide, CuBr_2 , *mp* 498 °C, d_4^{25} 4.77, crystallizes from warm solution as black, deliquescent, monoclinic crystals. Below 29 °C, the green tetrahydrate, $\text{CuBr}_2 \cdot 4\text{H}_2\text{O}$, results. The anhydrous product is very soluble in water (55.7 g/100 g solution) and soluble in ethanol and acetone. It is insoluble in diethyl ether, benzene, or concentrated sulfuric acid. Copper(II) bromide is most conveniently prepared by dissolving copper(II) oxide in hydrobromic acid; it can also be prepared by the direct action of bromine water on metallic copper. Copper(II) bromide is used as a brominating reagent and catalyst in organic synthesis and as an intensifier in photography.

Copper(II) chromate(VI), CuCrO_4 , is obtained as reddish brown crystals. Numerous insoluble basic salts can be formed from solu-

tions. Neutral copper(II) chromate is prepared by direct heating of a mixture of copper(II) oxide and chromium(VI) oxide. It decomposes around 400 °C, with the formation of copper(II) chromate(III). Copper(II) chromate(VI) is used in wood preservation and in the weatherproofing of textiles.

Copper(II) chromate(III), CuCr_2O_4 , forms black, tetragonal crystals which are insoluble in water. It is prepared by heating neutral copper(II) chromate(VI) to 400 °C. Copper(II) chromate(III) is used as a hydrogenation catalyst.

Copper(I) cyanide, CuCN , *mp* 474 °C (in nitrogen), d_4^{25} 2.92, is usually a white to cream-colored powder, which is practically insoluble in water, cold dilute acids, and ethanol, but dissolves in ammonia and alkali cyanide solutions with the formation of complexes. Copper(I) cyanide is produced by the addition of an alkali cyanide and sodium hydrogensulfite to a solution of copper(II) sulfate:



Copper(I) cyanide is very poisonous and must be handled cautiously. It is used in electroplating and in organic reactions as a polymerization catalyst or as a means of introducing the cyanide moiety. Copper(I) cyanide has also been used as an antifouling pigment for marine paints and is an active fungicide and insecticide.

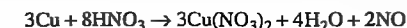
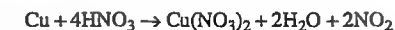
Copper(II) formate, $\text{Cu}(\text{HCOO})_2$, *mp* ca. 200 °C (decomp.), d_4^{25} 1.831, is soluble in water and slightly soluble in ethanol. The reaction of copper(II) oxide, carbonate, or hydroxide with formic acid is used to prepare the product. The most common commercial form, a royal blue material, is prepared by crystallization from water at 75–85 °C. A metastable dihydrate is produced by crystallization at 50–60 °C. Copper(II) formate tetrahydrate is prepared by crystallization from cool solutions. Copper(II) formate is used to prevent bacterial and mildew growth in cellulosic materials.

Copper(I) iodide, CuI , *mp* 605 °C, *bp* 1290 °C, d_4^{25} 5.62, occurs in nature as the mineral marshite, white to reddish brown cubic crystals. It is virtually insoluble in water but dissolves in ammonia solution, alkali iodide and cyanide solutions, and dilute hydrochloric acid. Copper(I) iodide is manufactured pyrometallurgically by the reaction of hot copper with iodine vapor. Alternatively, copper(II) salt solutions are reacted with alkali iodides to precipitate copper(I) iodide.

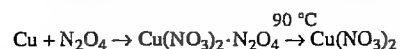
Copper(I) iodide is used as a heat and light stabilizer in polymers, photographic emulsions, and light-sensitive papers, and in oil drilling to aid in corrosion inhibition in highly acid environments. It is also used as a feed additive, in cloud seeding, and as a double salt with mercury(II) iodide as a temperature indicator.

Copper(II) nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, *mp* 114.5 °C, d_4^{25} 2.32, is a blue, deliquescent salt that crystallizes as rhombic plates. It is very soluble in water (77.4 g/100 g solution) and ethanol. When crystallized from solution below the transition point (26.4 °C), the hexahydrate is produced, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, *mp* 26.4 °C (with loss of 3 mol of water of hydration), d_4^{24} 2.07, blue, deliquescent, prismatic crystals. The anhydrous nitrate is not produced by heating the hydrates; instead, decomposition to the basic copper(II) nitrate, $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$, begins around 80 °C. Conversion to copper(II) oxide is complete at 180 °C.

Copper(II) nitrates are obtained by dissolving copper(II) oxide, basic copper(II) carbonate, or copper(II) hydroxide in nitric acid solution. The various hydrate crystals obtained depend on the conditions of crystallization. Basic copper(II) nitrate can be precipitated directly from solution by neutralization. Copper(II) nitrate salts are often produced by dissolving copper metal in nitric acid solution. The reaction is vigorous, and oxides of nitrogen are evolved:



The second reaction is favored by a lower temperature and dilute acid. Anhydrous copper(II) nitrate can be produced in ethyl acetate:



It is not available commercially.

The hydrates of copper(II) nitrate are used in the textile industry as oxidants and mordants in dyeing. They are used to prepare a copper(II) oxide of high surface area, which is useful as a catalyst in numerous organic reactions. The nitrate salts are used as colorants in ceramics, in the preparation of light-sensitive papers, and in the burnishing of iron, as well as the browning of zinc and brightening of aluminum. They are also used in pyrotechnics and as an oxidative component in solid rocket fuels.

Copper(II) oxalate, CuC_2O_4 , is a blue-white powder, which is very slightly soluble in water. Copper(II) oxalate is prepared by precipitation from a mixture of a copper(II) salt and sodium oxalate solution. The product is used as a stabilizer for acetylated polyformaldehyde and as a catalyst in organic reactions.

Copper(II) phosphate trihydrate, $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, is a light blue powder which is insoluble in cold water, slightly soluble in hot water, and soluble in ammonia solution and mineral acids. This compound is prepared by reaction of copper(II) sulfate solution with soluble alkali phosphates; it precipitates as a voluminous, almost gelatinous, product. Copper(II) phosphate trihydrate is used as a fungicide and corrosion inhibitor.

Copper(II) diphosphate hydrate, $\text{Cu}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ (variable), has the following typical analysis: Cu 33–36%, P_2O_7 45–49%. Copper(II) pyrophosphate is a light blue powder which is insoluble in water, but soluble in solutions containing an excess of diphosphate. It is prepared by the precipitation reaction of solutions of copper(II) sulfate and alkali diphosphate. Solutions are used for plating copper on plastics, aluminum, and zinc.

Copper(II) selenide, CuSe , mp not defined, d_4^{25} 6.0, decomposes at dull red heat; it is in-

soluble in water but dissolves in hydrochloric acid with evolution of H_2Se . Copper(II) selenide is prepared by reducing copper(II) selenite with hydrazine. It is used as a catalyst in the digestion of organic chemicals by the Kjeldahl method.

Copper(II) soaps are water-insoluble copper salts of long-chain fatty acids. They are usually sold as 6–10% copper solutions in a kerosene diluent. The copper(II) soaps are commonly prepared by direct reaction of the fatty acid with copper(II) hydroxide or basic copper(II) carbonate in an organic diluent, or by precipitation from aqueous media when copper(II) sulfate solution is mixed with the sodium salt of the respective fatty acid. The common commercially available soaps, concentrations, and uses follow.

Copper(II) naphthenate contains 8% copper and is used as a mildewcide in textiles, woods, and paints, and to prevent barnacle growth on ship bottoms.

Copper(II) oleate (9-octadecenoate) contains between 6 and 9% copper, and is used as a combustion improver in fuel oils, as an emulsifier and dispersant, and as an antifouling coating for fish nets and lines.

Copper(II) stearate (octadecanoate) contains 10% copper, and is used in antifouling paints and in the preservation of wood and textiles.

Copper(I) sulfide, Cu_2S , mp 1100 °C, d_4^{25} 5.6, occurs in nature as the mineral chalcocite, blue to gray rhombic crystals, also known as copper glance. It has a lustrous metallic look. Copper(I) sulfide is virtually insoluble in water, but is soluble with decomposition in nitric acid and concentrated sulfuric acid, and soluble in alkali cyanide solution through complex formation. It is decomposed to copper(II) oxide, copper(II) sulfate, and sulfur dioxide by heating in air, and to copper(II) sulfide and copper by heating in the absence of air. Copper(I) sulfide is prepared by heating copper and sulfur in a hydrogen atmosphere or by precipitation with hydrogen sulfide from an ammoniacal copper(II) salt solution. It is used in

luminous paints, lubricants, solar cells, thermoelements, and semiconductors.

Copper(II) sulfide, CuS , d_4^{25} 4.6, decomposes at 220 °C and occurs in nature as the mineral covellite, as blue-black hexagonal or monoclinic crystals. It is virtually insoluble in water, but soluble in alkali cyanides and in ammonia solution with complex ion formation. This compound is decomposed by hot nitric acid. It is stable in dry air, but is slowly oxidized to copper(II) sulfate in moist air. Copper(II) sulfide can be prepared by melting an excess of sulfur with copper(I) sulfide or by precipitation with hydrogen sulfide from a solution of anhydrous copper(II) chloride in anhydrous ethanol. It is used in the dye industry for the preparation of aniline black dyes and as an antifouling pigment.

Copper(II) tetrafluoroborate, $\text{Cu}(\text{BF}_4)_2$, is prepared commercially by the neutralization of tetrafluoroboric acid with copper(II) hydroxide or basic copper(II) carbonate. It is generally produced as a concentrated solution and is used in the production of printed circuits and in copper plating.

Copper(I) thiocyanate, CuSCN , mp 1084 °C (under nitrogen), d_4^{25} 2.84, is a white to yellow amorphous powder, which is very slightly soluble in water and dilute mineral acids, and soluble in ammonia solution, alkali thiocyanate solutions, and diethyl ether. It is stable to dry air but slowly decomposes in moist air. The material is prepared by reacting a copper(I) chloride solution with an alkali metal thiocyanate at 80–90 °C. The recovered product is dried under nitrogen. Copper(I) thiocyanate is used as an antifouling pigment.

8.11.4.2 Complexes

Copper(I) and copper(II) ions form many stable complexes with halides, amines, azo compounds, cyanides, and other complexing media. This, in part, accounts for the fact that more X-ray crystal structures have been determined for copper complexes than for any other first-row transition metal ion. Many of these complexes are of great commercial sig-

nificance. The dissociation constants for a number of copper complexes are given in Table 8.31.

Table 8.31: Dissociation constants of copper(I) and copper(II) complexes ($pK = -\log K$).

Complex ion	Dissociation products	pK
$[\text{CuCl}_3]^-$	$\text{CuCl} + 2\text{Cl}^-$	−2.0
$[\text{CuCl}_2]^-$	$\text{Cu}^+ + 2\text{Cl}^-$	4.7
$[\text{CuBr}_2]^-$	$\text{CuBr} + \text{Br}^-$	−3.3 to −2.3
$[\text{CuBr}_2]^-$	$\text{Cu}^+ + 2\text{Br}^-$	5 to 6
$[\text{Cu}(\text{CN})_3]^{2-}$	$[\text{Cu}(\text{CN})_2]^- + \text{CN}^-$	11.3
$[\text{Cu}(\text{CN})_2]^-$	$\text{Cu}^+ + 2\text{CN}^-$	16
$[\text{Cu}(\text{NH}_3)_2]^+$	$\text{Cu}^+ + 2\text{NH}_3$	10.8
$[\text{Cu}(\text{NH}_3)]^{2+}$	$\text{Cu}^{2+} + \text{NH}_3$	4.1
$[\text{Cu}(\text{NH}_3)_2]^{2+}$	$\text{Cu}^{2+} + 2\text{NH}_3$	3.5
$[\text{Cu}(\text{NH}_3)_3]^{2+}$	$\text{Cu}^{2+} + 3\text{NH}_3$	2.9
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$\text{Cu}^{2+} + 4\text{NH}_3$	2.1
$[\text{Cu}(\text{NH}_3)_5]^{2+}$	$\text{Cu}^{2+} + 5\text{NH}_3$	−0.5
$[\text{CuCl}_4]^{2-}$	$[\text{CuCl}_3]^- + \text{Cl}^-$	0.01
$[\text{CuCl}_3]^-$	$\text{CuCl}_2 + \text{Cl}^-$	0.06
CuCl_2	$\text{CuCl}^+ + \text{Cl}^-$	0.4
CuCl^+	$\text{Cu}^{2+} + \text{Cl}^-$	1
$[\text{Cu}(\text{OH})_4]^{2-}$	$[\text{Cu}(\text{OH})_3]^- + \text{OH}^-$	0.9
$[\text{Cu}(\text{OH})_3]^-$	$\text{Cu}(\text{OH})_2 + \text{OH}^-$	−5

Copper Ammine Complexes. Copper(II) salts form complexes of the type $[\text{Cu}(\text{NH}_3)_n]^{2+}$ where $n = 1-5$. The pentaammine complex is favored only in concentrated ammonia solution (Table 8.31). The hexaammine complex is formed only in anhydrous ammonia. The tetraammine complex of copper(II) is favored at low ammonia concentrations. For the copper(I) complexes of ammonia, the diammine complex is favored. Tetraammine copper(II) hydroxide, $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$, Schweizer's reagent, is used in the dissolution of cellulose and in the production of rayon. Copper(I) diammine salt solutions are used in the absorption of olefins and carbon monoxide. Many copper circuit boards are etched with ammoniacal ammonium salt solutions; copper ammine solutions, which can be used in the production of copper compounds, are by-products of this process.

Copper Chloride Complexes. Copper(I) and copper(II) ions form complexes with hydrochloric acid or soluble metal chlorides. Dilute solutions of copper(II) chloride are blue. As

the chloride concentration increases, the color of the solution shifts toward green, intensifying as the concentration of the distorted tetrahedral $[\text{CuCl}_4]^{2-}$ ion increases. Copper(II) compounds have been isolated that contain either the $[\text{CuCl}_4]^{2-}$ anion or the $[\text{CuCl}_3]^-$ anion, e.g., CsCuCl_4 and KCuCl_3 , respectively.

The insoluble copper(I) chloride can be solubilized by chloride-containing solutions, with the formation of the $[\text{CuCl}_2]^-$ ion. The benzene-insoluble copper(I) chloride dissolves readily in the presence of anhydrous aluminum chloride with formation of the $\text{Al}[\text{CuCl}_4]$ complex. In acetonitrile, copper(I) chloride is solubilized with the formation of the isolable $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{Cl}$ complex.

Copper(I) Cyanide Complexes. Alkali cyanides readily dissolve copper(I) cyanide, with the formation of $[\text{Cu}(\text{CN})_2]^-$ and $[\text{Cu}(\text{CN})_3]^{2-}$ complexes. Solutions or the complexes are of great importance in the electroplating industry because of their versatility. From saturated copper and sodium cyanide baths, crystals of the double salt $\text{Na}_2\text{Cu}(\text{CN})_3 \cdot 2\text{H}_2\text{O}$ can be obtained readily.

Other Copper Complexes of Industrial Significance. Solvent extraction of copper(II) ions relies on the ability of copper to form complexes and to break those complexes as a function of pH [337, 353, 354]. The most common reagents used commercially are substituted salicylaldoximes, 1,8-hydroxyquinolines, and α -hydroxyoximes.

Copper(II) is solubilized in alkaline media by complex formation with tartrates for use as Fehling's solution, which is utilized in the analysis of reducing sugars. Copper(II) *bis*-(1,8-dihydroxyquinoline) is used as a textile fungicide and as a pigment. Copper phthalocyanines [355, 356] are exceptionally stable blue and green pigments, as are the azo dye complexes of copper.

8.11.5 Reclamation

The reclamation or recycling of copper wastes and by-products is environmentally imperative and, in many cases, economically

sound. Better technologies have been developed to produce useful materials from wastes and by-products, many of which are now considered hazardous wastes. The establishment of the Resource Conservation and Recovery Act by the EPA defined procedures to assure proper disposal or reclamation of hazardous wastes [357]. However, no distinction is made between waste buried in an approved landfill and waste recovered as useful products. Unfortunately, in many cases this encourages the burial of recyclable waste materials.

The largest sources of reclaimable by-product copper are the electronics and plating industries, as well as spent electrowinning baths [340]. Electrowinning baths are most often crystallized or precipitated as tribasic copper(II) sulfate for use in agriculture.

In the manufacture of circuit boards, a copper laminate is selectively dissolved (etched). This dissolution process yields the desired circuit board and a by-product copper solution, the spent etchant. The earliest etching solutions used iron(III) chloride-hydrogen chloride or chromium trioxide sulfuric acid solutions which were difficult to recycle. Later, the sulfuric acid etchants that used hydrogen peroxide [358, 359] or persulfate [360-362] as oxidants were developed. Recycling of the copper is achieved through crystallization, precipitation [362], ion exchange [363], or cementation [364, 365]. Alkaline etchants utilized a mixture of ammonia and ammonium sulfate with persulfate as the oxidant [366] or a mixture of ammonia and ammonium chloride with chlorite as the oxidant [367]. The primary etchants used today are the ammonia ammonium chloride system with air as the oxidant and the hydrochloric acid system with stabilized hydrogen peroxide as the oxidant [368].

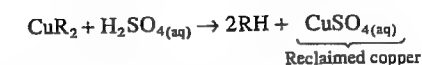
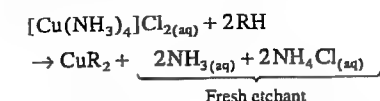
Copper is recovered from the acid chloride etchants:

- By neutralization and precipitation of copper(II) oxychloride or copper(II) oxide [262]
- By reduction with sodium hydrogensulfite, for example, to precipitate copper(I) chlo-

ride which can then be converted to copper(I) oxide by sodium hydroxide treatment [369]

- By cementation with scrap iron [370]. From the alkaline etchants, copper is recovered:
- By distillation to strip ammonia and precipitate copper(II) oxide [371]
- By addition of base to precipitate copper(II) hydroxide, followed by steam stripping of the ammonia [372]
- By reduction to copper with formaldehyde [373] or $\text{Na}_2\text{S}_2\text{O}_4$ [374]
- By electrolysis [375].

One of the more elegant methods for the recovery of copper from ammonia ammonium chloride etchants utilizes solvent extraction [376] (Figure 8.35). Not only is the copper recovered, but the etchant is simultaneously regenerated:



where R is an α -hydroxyoxime as shown by equation (1).

The copper can be further reclaimed by crystallization or electrowinning.

8.11.6 Copper and the Environment

The reclamation of copper by-products and wastes and the regulation of plant effluents and sanitary waters have resulted in lower indiscriminate release of copper into natural waters [377]. Where large quantities of copper in high concentration exist, recovery of the copper can, in many cases, be economical. Regulations have been established to control or limit altogether the introduction of copper into waters [378-382]. The Federal Water Pollution Control Act Amendments of 1972 set up a comprehensive program to "restore and main-

tain the chemical, physical, and biological integrity of the nation's waters" [378].

Limitations of copper in drinking water have also been established: the World Health Organization recommends 0.05-1.5 mg/L [383]. No specific drinking water standards for copper have been established by the Environmental Protection Agency [384].

A variety of technologies presently exist for the removal of copper from wastewaters and drinking water [385, 386]. The most common treatment methods include direct precipitation [378-380, 387-390] or electrolysis [391, 392].

Although copper is toxic in exceedingly low concentrations to certain lower life forms, notably fungi and algæ, it is a necessary constituent of higher plants and animals. Copper plays a necessary role as an oxidation catalyst and oxygen carrier, probably second only to iron in importance [393]. Copper aids plants in photosynthesis and other oxidative processes. In higher animals, it is responsible for oxidative processes and is present in many proteins such as phenolase, hemocyanin, galactose oxidase, superoxide dismutase, ceruloplasmin, tyrosinase, monoamine oxidase, and dopamine β -hydroxylase [394, 395].

Copper compounds are regularly applied for their nutrient value to agricultural crops in European countries [396-398]. In the United States, more emphasis is now being placed on the value of copper as a nutritional feed additive [396, 399, 400]: it increases the rate of gain and feed efficiencies of the animals. The increased use of copper as a feed additive has caused concern about the environmental impact of high levels of copper in manure [401, 402]. The recently approved maximum total copper content in animal feeds for Western European countries is shown in Table 8.32 [396].

Table 8.32: Maximum copper levels in Western European animal feeds.

Use	Total copper, mg/kg
Fattening pigs, up to 16 weeks	175
Fattening pigs, 17th week to 6th months	100
Fattening pigs, over 6 months	50
Breeding pigs	50
Calves, fed milk-based products	30
Calves, other feeds	50
Sheep	20
Other animals	50

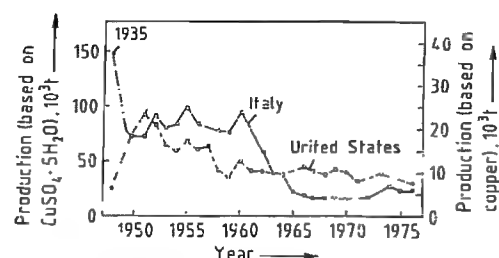
The largest single application of copper compounds is as an agricultural fungicide. Although copper is a necessary constituent of higher plants and animals, it is highly toxic to certain fungi. In human medicine, the importance of copper as a nutrient in proper development and growth is receiving increased study [394, 403]. Also, copper is being used in the production of new copper antibiotics and copper anti-inflammatory drugs [403]. The recommended daily requirement of copper is as follows [403]:

Humans	2.5–5.0 mg
Cattle	50–70 mg
Horses	50–60 mg
Sheep	10–15 mg
Swine	10–20 mg

8.11.7 Economic Aspects

The world's production of copper compounds represents less than 2% of the total production of primary metal [285]. In 1974, 7.65×10^6 t of primary copper was produced, with 1.3% (100 000 t) used in the production of copper compounds. Of these 100 000 t, 80% is used to prepare copper(II) sulfate pentahydrate.

Historically, the United States and Italy have led the world in producing copper sulfate pentahydrate (Figure 8.36) [285]. The U.S. production and valuation of copper sulfate pentahydrate are given in Table 8.33 [404].

**Figure 8.36:** Production of copper(II) sulfate pentahydrate in Italy and the United States (1950–1976).**Table 8.33:** Production and valuation of copper(II) sulfate pentahydrate in the United States.

Year	Production		Price of copper(II) sulfate pentahydrate, US\$/kg
	Quantity, t	Copper content, t	
1978	31 800	8551	1.04
1979	35 005	9286	1.18
1980	31 010	8445	1.23
1981	35 640	9413	1.14
1982	32 230	8385	1.08

Table 8.34: Estimate of current annual use of copper in agriculture [396].

Country	Total, t	Fungicide, %	Animal feed, %	Crop nutrient, %
Europe				
France	5 380	83.6	14.9	0.9
Germany	2 800	35.7	28.6	35.7
Greece	1 410	97.9	1.4	0.7
Italy	6 220	96.5	3.2	0.3
Portugal	1 120	89.3	8.9	1.8
Spain	2 800	89.3	10.7	0.0
Others	15 563	49.8	34.5	15.8
Asia and Australia				
Australia	1 556	19.3	6.4	74.3
India	3 500	0.0	0.0	100.0
Japan	2 040	98.0	1.2	0.7
Others	1 811	78.7	0.6	20.3
Africa				
Algeria	1 750	100.0	0.0	0.0
Kenya	1 000	100.0	0.0	0.0
Tanzania	2 000	100.0	0.0	0.0
Others	2 635	96.4	0.6	3.0
America				
Brazil	7 160	97.8	1.4	0.8
Mexico	1 650	100.0	0.0	0.0
United States	6 400	46.9	9.4	43.8
Others	3 540	40.7	2.8	56.6
Total	70 305	76.4	12.1	11.4

According to estimates about 70% (70 000 t) of the total world's production of copper compounds is used in agriculture [396]. Table 8.34 gives a breakdown by region, country,

and use. Copper sulfate pentahydrate can be blended directly with feed or fertilizers for animal feeds or crop nutrients, respectively. For application as a foliar fungicide, it must be rendered insoluble to prevent it from being easily washed off the leaf. The first copper fungicide on the market was Bordeaux mixture (1882), a combination of lime and copper sulfate [405]. The inherent phytotoxicity of Bordeaux mixture led to the development of the "fixed coppers" in the 1920s and 1930s. The fixed coppers are grouped into four categories: (1) basic sulfates, (2) basic chlorides, (3) oxides, and (4) miscellaneous — silicates, phosphates, etc. [406, 407]. To enhance their performance, the fixed coppers are usually blended with wetting agents, dispersants, sticking agents, and diluents. Since better coverage and enhanced efficacy are obtained with smaller particles, the basic coppers are usually ground before packaging [408]. Table 8.35 gives a partial list of available fixed copper fungicides.

8.11.8 Toxicology and Occupational Health

Copper is an essential trace element in humans. In larger quantities it can be lethal. The salts are usually considered to be more toxic than the metal. The acute oral toxicity in humans, LD_{50} , is about 100 mg/kg; however, recovery has occurred after ingestion of up to 600 mg/kg. The symptoms of copper poisoning include nausea, vomiting, gastric disturbances, apathy, anemia, cramps, convulsions, coma, and death.

Many reported cases of illness were once attributed to chronic copper poisoning, but they are now thought to be caused by impurities in the refining of copper, e.g., lead, arsenic, and selenium [409, 410]. The question of chronic poisoning is still open to debate. Prolonged exposure to copper dust can cause

skin irritation and discoloration of skin and hair. Whether pathological changes occur is uncertain, although there is evidence of accumulation of copper in the liver. Attempts to induce chronic copper poisoning in animals have been unsuccessful.

The inhalation of dusts of copper compounds irritates the upper respiratory tract [411, 412]. Ulceration and perforation of the nasal septum have occurred. Workers exposed to dusts of copper salts complained of metallic tastes and irritation of the oral and nasal mucosa. Smokers complained of an intense sweet taste during inhalation of the smoke. Long-term exposure to copper-containing dust has resulted in atrophic changes in the mucous membranes. Mild nasal discomfort was noted in workplace concentrations as low as 0.08 mg/m³. A very small fraction of the workers exhibited allergic skin reactions from exposure to copper-containing dust [413, 414].

Copper compounds embedded in the eye produce a pronounced foreign body reaction with discoloration of the ocular tissue. Conjunctivitis, ulceration, and turbidity have been reported [415, 416].

The current workplace standard for copper dust concentration in air, MAK and TLV, is 1 mg/m³ [417–419]. Copper fume standards are 0.2 mg/m³ [417] and 0.1 mg/m³ [418, 419]. A number of reviews and books of a more specific nature report detailed animal and workplace studies [420–424].

8.12 Copper Pigments

Copper and gold bronze pigments (powdered copper–zinc alloys) are usually produced by dry milling. Depending on the alloy composition, the following "natural shades" are produced:

Copper	100% copper
Pale gold	ca. 90% copper and 10% zinc
Rich pale gold	ca. 85% copper and 15% zinc
Rich gold	ca. 75% copper and 25% zinc

Table 8.35: Commercially available fixed coppers.

Manufacturer/representative	Trade name	Active ingredient	Cu, %
BASF	BASF-Grünkupfer	copper oxychloride	45
	Kauritil	copper oxychloride	47
Bayer	Cupravit-Spezial	copper oxychloride	45
	Cupravit-Forte	copper oxychloride	50
CP Chemicals	Basic Copper Sulfate	tribasic copper sulfate	53
	Champion WP	copper hydroxide	50
Cuproquim	Hydrox	copper hydroxide	50
Hoechst	Vitigran, Conc.	copper oxychloride	45
Kocide/Griffin	Kocide 101	copper hydroxide	50
Merck	Perenox	copper(I) oxide	50
Norddeutsche-Affinerie	Cobre Nordox	copper(I) oxide	50
Phelps-Dodge	Tribasic Copper Sulfate	tribasic copper sulfate	53
Sandoz	Cobre Sandoz	copper(I) oxide	50
Simplot	Blue Shield	copper hydroxide	50
Spiess Urania	Funguran	copper oxychloride	45
	Cuprasol	copper oxychloride	50
Tennessee Copper	Tribasic Copper Sulfate	tribasic copper sulfate	53
Wacker	Wacker-Kupferkalk	copper oxychloride	15-18

Copper-zinc alloys with a higher zinc content (brass) cannot be ground or formed into flake pigments on account of their brittleness. Controlled oxidation of "natural" bronze powders converts them into "fired" bronze powders. These shades (e.g., English green, lemon, ducat gold, fire red) are produced as a result of interference effects that depend on the thickness of the oxide coating.

Copper and gold bronze pigments are not as colorfast as aluminum pigments because they decompose to produce colored oxides and corrosion products. However, stabilized pigments (e.g., with a silica coating) are also available for critical applications in binders with high acid values or that react with copper or zinc.

The classical fields of application for the gold bronze pigments are the graphics industry (bronzing); printing (offset, gravure, flexographic, and screen printing); and coloring plastics. They are also used in the paint industry for decorative finishes (e.g., dip coatings for candles).

Gold bronze pigments are nontoxic. In Germany they are permitted in food packaging materials provided that they do not lead to contamination of the food. They are also allowed for printing on cigarette paper and filter tips according to the tobacco regulations if the zinc content does not exceed 15%. Similar

regulations apply in the United States and other countries.

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9 Lead

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9.1 Introduction

The metal lead remains a major nonferrous commodity in modern industry as it has been from antiquity. In 1988 lead consumption in the nonsocialist world was estimated to be 4.2×10^6 t, which is well below the capacity of the primary producing and recycling plants. Con-

cern about the toxicity of lead has brought about substitutions in some uses and proscriptions in others; consequently, the lead market is now dependent on the lead storage battery. Growth in the transportation field, principally in conventional internal combustion engine automobiles, has been the main factor in sustaining a modest growth in lead consumption

of around 2.4% in 1988. The consumption of lead in other use areas (including the drastically reduced gasoline additive market, pigments, ammunition, solders, plumbing, and shielding) amounts to less than that in the battery market. Recent discoveries in North America, Australia, South Africa, and China have brought economic lead ore reserves to a level comfortably above expected consumption.

9.2 History

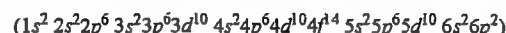
The knowledge and use of lead goes back as far as 5000 B.C. to the ancient Egyptians. The metal was used extensively by the Phoenicians, Romans, Indians, and Chinese. The first lead mines in Spain were operated around 2000 B.C. The uses of the metal included weight standards, coinage (ultimately replaced by silver), statuary, sheathing and lining, trinkets, anchoring of iron rods, and making of seals. The Greeks operated lead mines at Laurium in the fifth century B.C. and the Romans mined in the Rio Tinto region of Spain in 300 B.C. The Romans used lead extensively for water piping; indeed latin "plumbum" for lead came from the word for a water spout, and from it has come the name plumber. They also used lead for soldering, in sheets for inscribed lettering, and for preparation of lead oxides. Lead uses increased in the Middle Ages with supporting mines appearing in England, Germany, Bohemia, and other parts of Europe. Lead roofing, lead "comes" in stained glass windows, guttering, drain pipes, and later type founding were additional uses that continue today. Lead received considerable attention from the alchemists. Older uses of lead as material for projectiles expanded considerably with the invention of firearms.

In the nineteenth century, the United States entered the lead production industry because of its major natural resources, and was followed by Australia and Canada. In the twentieth century the appearance of the automobile, chemical, and machine industries created large new uses for lead in gasoline antiknock

additives, bearing and plumbing alloys, accumulator batteries, and chemical equipment. Modern uses include glass making, sound attenuation, and radiation shielding.

9.3 Properties

The element lead is a lustrous metal. When freshly cut, surfaces are bluish white but oxidize readily to the familiar dull grey color. Lead is located in group 14 of the periodic table. The element displays valences of 2+ and 4+ as indicated by its electronic configuration:



This permits attainment of stability by donation of two or four electrons.

Lead Isotopes. Lead (atomic number 82) has four naturally occurring isotopes; mass numbers listed in order of abundance are 208 (51–53%), 206 (23.5–27%), 207 (20.5–23%), and 204 (1.35–1.5%). Variations in isotopic concentration can cause a difference of 0.15 in the normal atomic mass A_r of 207.21. Three of the natural isotopes are radioactive: ^{208}Pb is the end product of thorium decay, while ^{206}Pb and ^{207}Pb are formed from the uranium series via actinium and radium, respectively. A number of unstable radioactive isotopes exist with mass numbers of 200–203, 205, 209–214. Lead is a preferred shielding material against gamma rays and X-rays because of its high density and atomic number; if sufficiently pure, it does not become radioactive when used for shielding against neutron sources.

Physical and Mechanical Properties. The outstanding physical properties of lead are its low melting point, high density, softness, and malleability. The metal can readily be worked by rolling and extruding, and is slightly ductile. The physical and mechanical properties of lead follow:

<i>Physical Properties:</i>	
<i>mp</i> , °C	327.4
Latent heat of fusion, J/g	23.4
<i>bp</i> , °C	1741
Latent heat of vaporization, J/g	862
Vapor pressure, kPa	
980 °C	0.133
1160 °C	1.33

1420 °C	13.33
1500 °C	26.7
1600 °C	53.3
<i>Density, g/cm³</i>	
20 °C	11.336
327.4 °C (solid)	11.005
327.4 °C (liquid)	10.686
400 °C	10.597
500 °C	10.447
<i>Mean specific heat, J g⁻¹ K⁻¹</i>	
–200–0 °C	0.1202
0–100 °C	0.131
0–200 °C	0.134
0–300 °C	0.136
<i>Specific electrical resistance, Ω/cm</i>	
20 °C	20.65
100 °C	27.02
200 °C	36.48
300 °C	47.94
<i>Thermal conductivity, W m⁻¹ K⁻¹</i>	
–100 °C	0.371
0 °C	0.355
100 °C	0.342
200 °C	0.329
300 °C	0.316
327.4 °C (solid)	0.313
327.4 °C (liquid)	0.155
<i>Surface tension of liquid lead, mN/m</i>	
327.4 °C	444
350 °C	442
400 °C	438
500 °C	431
600 °C	424
800 °C	410
<i>Dynamic viscosity of liquid lead, mPa·s</i>	
327.4 °C	2.75
350 °C	2.60
400 °C	2.34
450 °C	2.12
500 °C	1.96
550 °C	1.70
<i>Magnetic susceptibility (20 °C), H m⁻¹ kg⁻¹</i>	
–1.5 × 10 ⁻⁹	
<i>Coefficient of linear expansion, K⁻¹</i>	
at 20 °C	29.1 × 10 ⁻⁶
mean 20–300 °C	31.3 × 10 ⁻⁶
<i>Mechanical Properties:</i>	
Brinell hardness (20 °C)	2.5–3.0
Transverse contraction coefficient (20 °C)	0.45
Young's modulus, GPa	16.5
Elongation (in 5-cm gauge length), %	50–60
Velocity of sound in lead, m/s	1227
<i>Tensile strength, kPa</i>	
–100 °C	42 000
20 °C	14 000
150 °C	5 000

Chemical Properties. Fresh cut or cast lead surfaces undergo oxidation and tarnish rapidly to form an insoluble protective layer of basic lead carbonate. Lead is attacked by water in the presence of oxygen, but again an insoluble carbonate or silicate protective layer is formed if dissolved carbonates or silicates are present in the water. This resistance of the metal to

corrosion by air, water, and soil has been exploited in the historical uses of lead in plumbing and piping. Lead might be expected to dissolve in acids with liberation of hydrogen, but this is prevented by the high hydrogen overvoltage, and attack occurs only when the combination of oxidizing conditions and soluble salt species exists. Thus the metal resists hydrochloric acid corrosion to quite high concentrations, sulfuric acid to 60 °Bé (ca. 13.3 mol/L), and hydrofluoric acid totally; however, it dissolves readily in warm, dilute nitric acid to form soluble lead nitrate. Lead is also corroded by weak organic acids, such as acetic or tartaric acid, in the presence of oxygen. The protective coating formed by oxidation is removed by alkali with formation of soluble plumbites and plumbates.

Crystal Structure. Lead crystals are face-centered and cubic with the following dimensions:

Atomic radius, nm	0.175
Atoms per unit cell	4
Lattice constant (edge of unit cell), nm	0.49389

Electrochemical Properties.

Electrochemical equivalent, g A ⁻¹ h ⁻¹	3.865
Ionic radius, Pb ²⁺ , nm	0.118
Pb ⁴⁺ , nm	0.070
Metallic radius, nm	0.17502
Covalent radius (sp ³), nm	0.144
<i>Ionization potentials, eV</i>	
1st	7.415
2nd	14.97
<i>Standard oxidation potentials (25 °C), V</i>	
Pb → Pb ²⁺ + 2e ⁻	0.126
Pb ²⁺ + 2H ₂ O → PbO ₂ + 4H ⁺ + 2e ⁻	–1.456
Pb + 2OH ⁻ → PbO + H ₂ O + 2e ⁻	0.576
Pb + 3OH ⁻ → HPbO ₂ ⁻ + H ₂ O + 2e ⁻	0.54

Lead forms two series of compounds corresponding to valence states of 2+ and 4+, lead(II) compounds are electrovalent (ionic), while those of lead(IV) are essentially covalent. The metal is amphoteric and forms lead salts, plumbites, and plumbates. When melted in air, lead oxidizes readily to its monoxide PbO (also called litharge or simply lead oxide); oxidation (drossing) can be promoted or inhibited by dissolved metallic impurities. Other lead oxides are the dioxide PbO₂ (actually sesquioxide Pb₂O₄) and red lead Pb₃O₄ (the orthoplumbate Pb·Pb₂O₄). All the lead(III) halides are known, and are consider-

ably more soluble in hot water than in cold they also form double chlorides with alkali metals and a series of oxyhalides, the oxychlorides being the most familiar. Other common compounds of lead are the soluble nitrate and acetate; lead chromate (chrome yellow) used as a pigment along with red lead; lead borate used along with oxides in glass making; lead sulfide (galena), which is the principal naturally occurring form of the metal; and lead sulfate that is readily formed by sulfating a soluble lead salt and by natural oxidation of galena.

9.4 Occurrence

Lead, like copper and zinc, is a markedly chalcophilic element. Its mean abundance in the Earth's crust is 16 g/t (0.0016%). Enrichments occur only in the pneumatolytic and especially the hydrothermal sulfide phase in the form of vein (lode), impregnated, and particularly metasomatic deposits. Sedimentary enrichments are of little importance.

Lead Minerals. Galena or lead sulfide, PbS, theoretically 86.6% Pb, is by far the most important lead mineral and the sole primary one. Other common forms of naturally occurring lead are usually associated with or derived from galena deposits. They include mixed sulfides such as jamesonite, $\text{Pb}_4(\text{Sb,Fe})_7\text{S}_{14}$ (ca. 40% Pb) and boulangerite, $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ (ca. 58% Pb); anglesite, PbSO_4 (68.3% Pb), a product of galena oxidation; cerussite or white lead ore, PbCO_3 (77.5% Pb), a decomposition product of galena; pyromorphite, also qualified as green, brown or variegated lead ore, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ (76% Pb); vanadinite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$; wulfenite or yellow lead ore, PbMoO_4 (56% Pb); crocoite, PbCrO_4 ; and phosgenite or horn lead, $\text{Pb}_2\text{Cl}_2\text{CO}_3$. Frequent impurities in lead minerals are zinc, copper, arsenic, tin, antimony, silver, gold, and bismuth.

Deposits. The most important mineable lead ore is galena, which occurs chiefly in association with other minerals, mainly zinc ores. Lead deposits can be classified as follows:

- Hydrothermal vein, impregnation, and replacement deposits (e.g., Broken Hill, Australia; Anvil Mine, Canada; and numerous deposits of the Cordilleran-Andean Orogeny);
- Volcanogenic sedimentary deposits, some occurring as massive bodies of rich ore, others as impregnations (e.g., Sullivan Mine, Canada; Rammelsberg, Germany; Mount Isa and Hellyer, Australia);
- Hydrothermal or marine sedimentary deposits, typically in calcareous or dolomitic formations of the North American and European platforms (e.g., Pine Point, Canada; the New Lead Belt in the Missouri district, United States; Red Dog, Alaska).

In world mining output, mixed lead-zinc ore deposits are most important and account for ca. 70% of total production of both metals. In second place are deposits that contain predominantly lead ores (ca. 20% of total production), and the remainder (ca. 10%) is obtained as a by-product from zinc, copper-zinc, and other deposits.

Table 9.1: World lead ore reserves (millions of tonnes contained lead) (U.S. Bureau of Mines, Division of Mineral Commodities, January 1989).

Country	Reserves ^a	Reserve base ^b
Australia	16	28
United States	11	22
Canada	8	15
South Africa	4	6
Mexico	3	4
Peru	2	3
Former Yugoslavia	2	3
Other market economy countries	9	14
Centrally planned economies	20	30
Total	75	125

^a Estimated currently economically recoverable lead.

^b Reserves augmented by marginally economic ores, some currently uneconomic but with potential, and also some provision made for determination of additional reserves in known ore bodies.

An important by-product of lead ore production is silver, which is incorporated into the lattice of galena, and is recovered with the lead when concentrates are smelted. Some 70% of world silver production comes from lead concentrates. Valuable amounts of gold

are also contained in some lead deposits. Another by-product from lead ore is copper, but the amount is a very small part of the total world copper output.

Reserves. Total world lead reserves were reported in 1987 as 75×10^6 t lead content (Table 9.1). Western countries owned about 73% of the total.

The United States has extensive lead deposits in the southeast of Missouri (New Lead Belt). These deposits and the new Red Dog lead-zinc orebody in Alaska are located in bedded marine-sedimentary or hydrothermal deposits. Further reserves are found in the Rocky Mountains (Idaho, Utah, Colorado) in the form of hydrothermal vein and replacement deposits. Canadian reserves are also substantial but of generally lower grade, and are located in the Appalachian region of New Brunswick, the Rocky Mountain trench, and the Yukon. North and South America, including the Latin American countries, hold about 35% of known reserves.

Australia has the most substantial lead resources amounting to about 21% of the world total; they are concentrated in Mount Isa (Queensland), Broken Hill (New South Wales), and Tasmania.

The remaining western reserves are found in many places in Europe, Africa, and Southern and Eastern Asia. The largest known European reserves are in Yugoslavia.

Most Eastern Bloc reserves (ca. 27% of world reserves) lie in the former Soviet Union (Kazakhstan and the Altai and Karatau regions). Only little information is available on these reserves and recent discoveries in China.

Data on exploitable reserves are only valid in the short-term, because they are subject to long-term economic fluctuations. The growth of world reserves of lead ore through new discoveries can be expected to outstrip the increase in primary metal production. Recycling of lead, already a major source of the metal, particularly for battery making, can be expected to suppress production from primary sources.

9.5 Production

9.5.1 Ore Concentration

The most common feed for lead production is sulfidic lead concentrate, which contains an average of 50–60% lead (occasionally as high as 70–80% or as low as 30%). Oxide lead concentrates are of secondary importance.

Lead ores in deposits are usually intergrown with other minerals and with host rock. These crude ores are not smeltable and must first be beneficiated into concentrates of much higher lead content but with minimum loss of lead.

Ore beneficiation normally includes crushing, dense-medium separation, grinding, froth flotation, and drying of concentrate. Lead flotation is usually the first step in the separation of lead-zinc and lead-zinc-copper ores.

9.5.2 Smelting

The major process for the production of primary lead from a sulfide concentrate is the sinter oxidation-blast furnace reduction route. Older processes involving direct oxidation of lead sulfide to lead or the roast reaction between lead sulfide and the oxidation products lead oxide and lead sulfate are now of little importance. In the last two decades new oxygen metallurgy processes featuring sulfide oxidation in a flash flame or by oxygen injection into a slag bath, followed by reduction of the lead oxide slag, have advanced to industrial application.

In the Imperial Smelting Furnace process, lead is produced simultaneously with zinc. This process will not be considered here, for details see Chapter 10.

9.5.2.1 Sintering Reduction Process

The sintering reduction process involves two steps:

- A sintering oxidative roast to remove sulfur with production of PbO

- Blast furnace reduction of the sinter product.

The objective of sintering lead concentrates is to remove as much sulfur as possible from the galena and the accompanying iron, zinc, and copper sulfides, while producing lump agglomerate of adequate strength combined with porosity for subsequent reduction in the blast furnace. The sulfur dioxide content of the sintering gases is often recovered and used in sulfuric acid production. The chemistry of the roast sintering process is complex because it involves many oxygen- and sulfur-containing lead compounds.

The Pb-S-O System. The Pb-S-O system was investigated comprehensively by KELLOGG and BASU [7] whose results were later confirmed by many investigators. WILLIS provides an excellent summary of the physical chemistry of the oxidation of lead sulfide [8]. Lead in sinter occurs mainly as lead monoxide or lead silicate. The temperature of the sinter charge must be high enough to attain the area of PbO predominance (i.e., > 950 °C, see Figure 9.1).

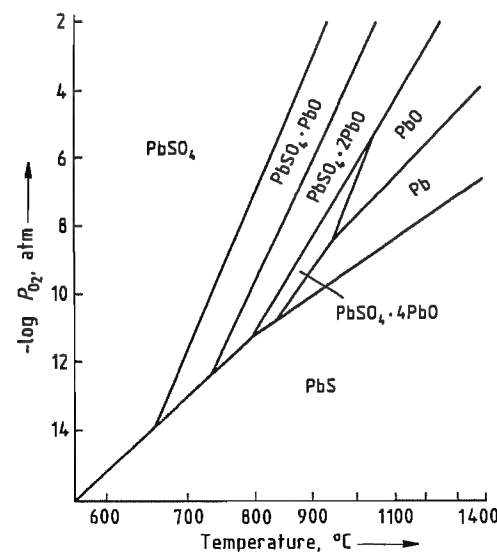


Figure 9.1: Phase relations in the Pb-S-O ternary system with air as the oxidizer and a partial sulfur dioxide pressure of 0.2 atm [9]. * 1 atm = 0.1013 MPa.

Oxidation starts with the formation of lead sulfate, which is the stable reaction product at the oxygen and sulfur dioxide partial pressures and temperatures commonly used in sintering. Lead sulfate then reacts further with lead sulfide, decomposing to increasingly basic sulfates and ultimately to lead monoxide. Lead in dust carried out by the sintering gas is totally sulfated.

The composition of the sinter is important as regards its behavior in the blast furnace. The lead monoxide and lead silicate which account for most of the lead content are readily fusible and reducible. The integrity of the sinter thus depends on the presence and quantity of other constituents, typically silicates of zinc, iron, and calcium, and ferrites. These substances are much more refractory than the lead compounds and provide a framework that keeps the sinter lump from disintegrating after the lead compounds have been removed.

Sinter Roasting Techniques. The development of sinter roasting goes back to work by HUNTINGTON and HEBERLEIN (1896), who proposed that lead ores mixed with limestone chips be roasted in a converter with an air blast (blast roasting). Implementation of this idea became the basis of the modern sintering technique, which combines roasting with agglomeration of the charge in the sintering step.

A continuous sintering machine with a sintering bell was devised in 1905–1908 by DWIGHT and LLOYD. At about the same time, von SCHLIPPENBACH introduced the circular sintering machine.

A distinction is made between *downdraft sinter roasting*, where the air required for roasting is drawn downwards through the sinter mixture, and *updraft sintering*, in which the air is blown upwards through the bed. Updraft sintering is preferred because it produces lower gas volumes of higher sulfur dioxide content that are suitable for sulfuric acid production.

Downdraft Sintering

The original downdraft process proposed by DWIGHT and LLOYD was the conventional

technique for the sinter roasting of lead ores until about 1955. It has now been superseded by updraft sintering. In downdraft sintering the nodulized charge blend is fed continuously onto a traveling grate, and sulfides are ignited on the surface of the charge bed by burners. As the ignited charge moves away from the ignition zone, air is drawn downward through the charge. The sulfur is burned on a downward advancing front, and incipient fusion of solids agglomerates the nodules of desulfurized charge into a porous sinter product.

A characteristic of downdraft sintering of lead ores is the low sulfur dioxide concentration of the roasting gases (Figure 9.2). Since off-gases containing 1–2 vol% sulfur dioxide occur at the end of the sintering machine and cannot generally be discharged into the atmosphere, recirculation of the gas or chemical scrubbing is necessary. Even with gas recirculation, the production of acid-strength gas causes problems due to the formation of liquid phases during sintering that reduce the gas permeability of the bed, and in particular to the metallic lead formed by the reaction of lead sulfide with lead sulfate. The molten lead flows downward through the sinter bed along with the gas stream and forms a very tight layer immediately above the grate. Part of the lead also drops through the grate into the wind boxes. Removal of the lead from the wind boxes is expensive and causes long downtimes. Water-bath quenching of wind-box lead and conveyor belt cleaning have been practised to overcome this problem. With downdraft sintering the maximum lead content of the sinter mix is limited to about 40% to avoid excessive production of wind-box lead.

Updraft Sintering

Principles. The difficulties encountered in downdraft sintering are avoided in updraft sintering in which sintering takes place in an ascending gas stream (Figure 9.3). Roasting air is supplied to the machine from below through

the wind boxes, and the gas flows upward through the sinter bed. To initiate roasting, a 2–3 cm layer of feed is placed on the grate and ignited in a downdraft ignition box (Figure 9.3A). The main sinter bed (d) is then distributed onto the burning ignition layer (b), the direction of gas flow is reversed (Figure 9.3B), and air is forced upward through the sinter bed. The main layer is ignited from the first layer, and sinter roasting advances upward. To prevent caking of the ignition layer on the grate bars during downdraft ignition, the grate is usually covered with a hearth layer of return sinter (c) before the ignition layer is placed.

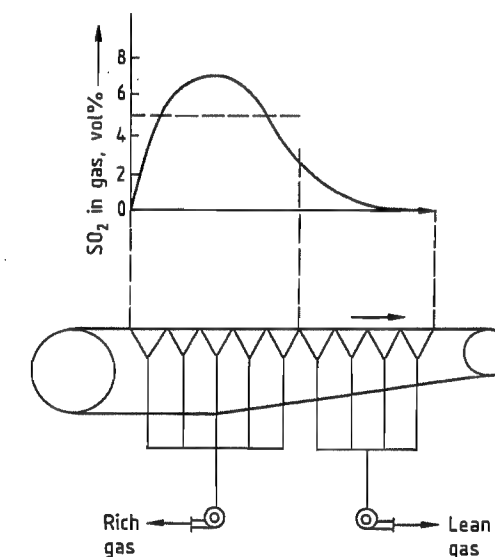


Figure 9.2: Variation in sulfur dioxide content of sintering gases along a downdraft sintering machine.

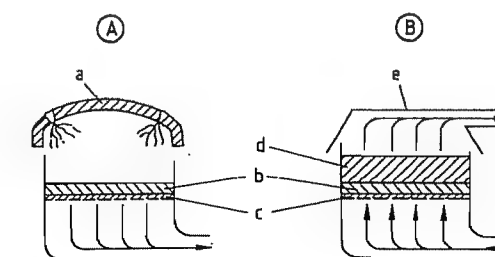


Figure 9.3: Updraft sintering. A) Downdraft ignition; B) Sintering. a) Ignition hood; b) Ignition layer; c) Hearth layer; d) Sinter bed; e) Exhaust hood.

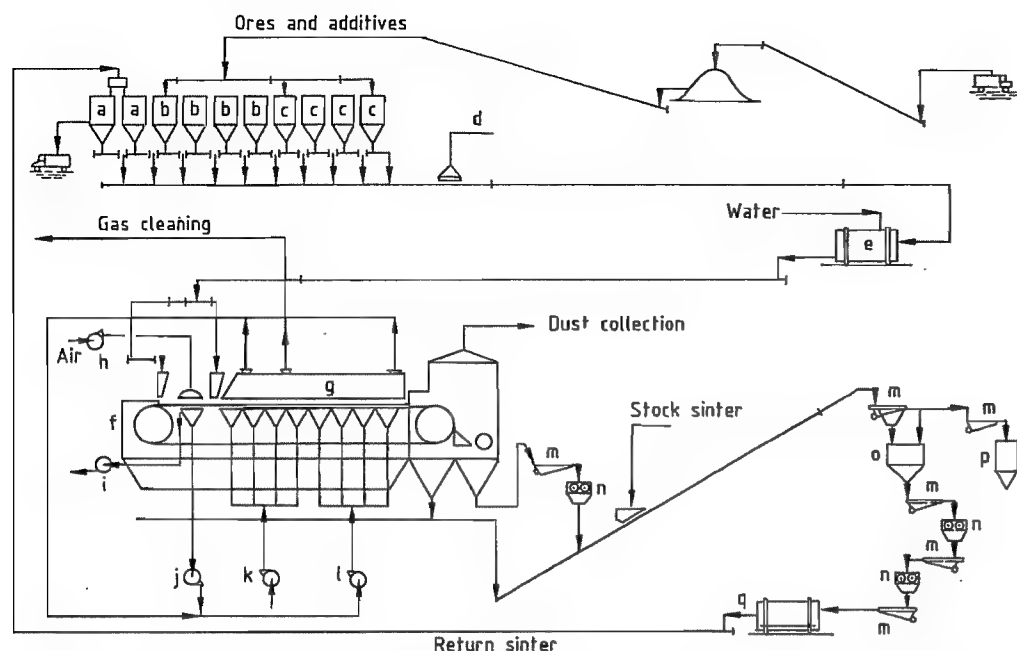


Figure 9.4: Flowsheet of an updraft sinter plant for lead ores: a) Return sinter bins; b) Lead concentrate bins; c) Flux and other charge material bins (silica, limestone, leach residues, etc.); d) Magnet; e) Mixing-nodulizing drum; f) Sinter machine; g) Sinter grate; h) Ignition air blower; i) Ventilation air blower; j) Ignition exhaust fan; k) Sintering air blower; l) Sinter gas recycle blower; m) Sinter screens; n) Roll crushers; o) Undersize sinter bin; p) Product sinter bin; q) Return fines cooling drum.

Since cold air flows into the sinter bed from below, any metallic lead that forms is immediately cooled and solidifies while still in the bed. This makes for good permeability of the bed, lower gas flow, and uniform sintering. Higher sulfur dioxide levels in the roast gases can thus be achieved, and sinter charges containing up to 50% lead can be managed.

Plant Design. The development of updraft sintering began in 1950–1955 at the Port Pirie lead smelter in Australia and at Lurgi Gesellschaft für Chemie und Hüttenwesen, Germany. The process has since been adopted worldwide. All recently constructed sintering plants have been designed for updraft sintering and a large number of downdraft plants have been reconstructed. Updraft sintering became an essential component of the Imperial Smelting zinc process because of the exacting requirements for satisfactory operation (i.e., low sulfur and high sinter hardness).

The flowsheet of a plant of modern design is shown in Figure 9.4. Recent developments have concerned not only increases in the size of updraft sintering machines, but also improvements in capacity, automation, and of working conditions. Dust-collection systems and gas-cleaning systems must comply with increasingly strict regulations on air and water pollution control.

An updraft sintering plant comprises many devices and machines, which employ a logical system of electrical interfaces. Precise control of process performance is difficult, primarily because lag times from entry of the feed to appearance of the product from the sinter strand are long and sampling of the feed and product sinter are difficult. Consistent feed preparation, either by means of large-scale bedding operations or very accurate weigh feeders for the concentrates and fluxes, can provide a high precision of feed-forward control.

Feed Mixture. A charge moisture content of 4.5–5.5% is of utmost importance for achieving good bed permeability during combustion. The desired moisture content of the feed mixture is attained by adding water to the tumbling and mixing drum. Two drums usually operate continuously to achieve good control. If feed material moisture is too high, charge drying is required.

Crushed recycle sinter is required to control the fuel content of the charge and to enhance bed permeability. Cooling of recycle sinter is necessary for mechanical reasons and to minimize dust production. The main difficulties encountered in return sinter cooling are caused by irregular discharge of the sinter strand combined with the handling of moist ventilation gases produced in water quench cooling drums.

Because sinter quality and plant capacity are strongly affected by the physical quality of the recycled sinter, comminution of the returns is very important. The desired size distribution of the lump sinter that is to be reduced in the blast furnace is obtained by two-stage crushing and screening. The returns needed for the sinter charge are also broken down to the requisite particle size (normally 6 mm) by using roll crushers in a two-stage process.

Dust Collection. Dust collection is a major problem in updraft sintering plants. The plant comprises many machines and devices, some of which must transport, screen, and crush hot material; lead-containing dust is produced at all transfer points. Proper ventilation is essential to provide satisfactory in-plant hygiene, and efficient cleaning of exhaust gas is required to control lead emissions. High volumes of ventilation air have to be handled at considerable extra cost. Dust recovered from baghouses and wet scrubbers must be recycled to the process.

Because sintering plants emit both dry and wet dust-laden gases, gas cleaning design has been constantly improved. The most recent plants employ a combination of wet scrubbing and dry baghouse gas cleaning. The cooling drum ventilation and the hot gases from the

sintering machine are cleaned in water scrubbers. Discharge gas temperatures are too high for bag filters. The other dust-collection points (crushing and screening) are combined in a common baghouse. Dust recovered from baghouses is added to the thickener slime that is supplied as coolant to the cooling drum. The dust load in the process sulfur dioxide from the sintering machine is usually collected in high-temperature electrostatic precipitators, moistened, and added directly to the sinter mixture.

Recovery of Sulfur. For optimal operation of the sintering machine, some 15–20 m³m⁻² min⁻¹ of air (at STP) must be delivered along its whole length. The combined exhaust gases have an average sulfur dioxide content of 4–5 vol%. However, since peak sulfur dioxide levels of over 10% occur at the front end of the sintering machine, a rich gas stream with a relatively high sulfur dioxide content can be separated and the balance tail gas is recycled to the front-end wind boxes. In this way, a rich gas containing 6–6.5 vol% sulfur dioxide can be delivered to a sulfuric acid plant. The technique involves a certain deliberate loss of capacity resulting from the injection of hot recycled lean gas at 300–350 °C.

Size and Capacity of Sintering Plant. Standard sizes have been adopted for updraft sintering machines. Size is defined chiefly by smelting capacity and by the quantity of sulfur to be combusted.

Roasting capacities of 1.3–1.5 td⁻¹m⁻² are achieved with modern updraft sintering and are over 50% higher than those of older downdraft systems. For normal lead sintering an annual lead production capacity of 70 000–100 000 t requires a sinter machine of 50–70 m² updraft area. Machines up to 90 m² are employed in Imperial Smelting process plants. These rates and sizes are material-dependent and must be confirmed by tests for each proposed charge. Data for the updraft sinter plant at Port Pirie, Australia are listed below:

Number of sinter machines	1
Roasting surface	
total, m ²	70.5
effective, m ²	62.3

Sinter production, tm^2d^{-1}	20.1
Throughput, t/d	4500
Feed blend, %	
new materials	36
return sinter	64
Sulfur content, %	
concentrates	16–27
new materials	11
return sinter	2.5
total feed blend	5.5
product sinter	1.8
Lead in sinter, %	45
Thickness of ignition layer, mm	35
Total bed thickness, mm	300
Strand speed, m/min	1.42
Ignition method	downdraft
Ignition burners	
number	2
fuel	natural gas
usage, m^3/h	30
Wind boxes	
number	9
bed area, m^2	4.9 (no. 1)
pressure, kPa	8.2 (nos. 2–9)
	5.0 (no. 1)
	4.5 (no. 2)
	3.5 (no. 3)
	2.0 (nos. 4–9)
maximum air flow, $\text{m}^3\text{min}^{-1}\text{m}^{-2}$	38.8
SO ₂ concentration, vol%	4–6
Sulfuric acid production	yes

Sintering for the Imperial Smelting Process. Lead-zinc concentrates or mixtures of lead and zinc concentrates for the Imperial Smelting Furnace process must be desulfurized and sintered before reduction in the zinc vaporizing blast furnace. The sinter must incorporate recycled intermediate products from the sinter plant and blast furnace and also the fluxes needed to obtain the desired slag balance. The sinter must be chemically uniform, well desulfurized, as well as hard and abrasion-resistant to avoid formation of lines in the furnace. It must also have a high porosity and a narrow particle-size range.

These requirements can be satisfied only by carefully controlled updraft sintering with feed sulfur held between 5 and 6.5%, moisture at 4–7% and return sinter sizing between 1 and 5 mm. For further details, see Chapter 10.

Products of Sinter Roasting

Sinter. Product sinter should be agglomerated in large lumps that are strong enough to prevent decrepitation during handling. The sinter

should have a cellular, porous structure without pockets of unroasted ore or very dense regions.

Sintering Gases. The sulfur dioxide concentration in the sintering gases is lower than that found in the roasting of zinc or copper ores, especially when high-lead concentrates containing as little as 14–16% sulfur are processed. In the sintering of lead concentrates, the sulfur dioxide level fluctuates between 4 and 6 vol% under favorable conditions and with gas recycling. Release of the lean gases into the atmosphere is unacceptable, although this is still done in a few instances. The roasting gases contain a small amount of sulfur trioxide; their dust content is usually 2–5 g/m^3 , but may reach 20 g/m^3 in exceptional cases. Extensive cleaning is always necessary if the gas is to be processed into sulfuric acid. Pollution control laws require that metal losses be kept to a minimum. The typical gas cleaning train consists of dry electrostatic precipitators, a wet scrubber, followed by wet electrostatic cleaning.

The cleaned sintering gases are generally forwarded to sulfuric acid production. They are sometimes processed into liquid sulfur dioxide after absorption in an organic solvent. In rare cases they are scrubbed with ammonia to produce ammonium sulfate and high-strength sulfur dioxide for recycle or liquid sulfur dioxide production.

Sulfuric acid derived from lead-sintering plants is produced as "black acid". Its black color is due to carbon particles from the volatile organic constituents of flotation reagents. The color can be removed with hydrogen peroxide at additional expense.

Flue Dusts. Flue dusts from lead sintering plants contain 60–70% lead, about 10% sulfur, and varying amounts of zinc, cadmium, arsenic, antimony, and mercury. The lead is predominantly in the form of lead sulfate or basic lead sulfate, with a minor quantity of lead sulfide. Flue dusts are recycled to the sinter blend.

9.5.2.2 Reduction in the Blast Furnace

The second part of the roast reduction process is carried out in a blast furnace. Where the lead content of the sinter (mainly lead oxide) is reduced to metallic lead, other metals such as copper, antimony, arsenic, and noble metals are also produced. Other constituents (gangues) contained in the sinter and the flux are carried off as silicate slag. In lead blast-furnace smelting, zinc remains in the slag, but in the Imperial Smelting process the furnace top is hot and gaseous zinc leaves the furnace along with the off-gases and is then condensed to liquid zinc metal.

The charge to the blast furnace comprises

- Sinter, which incorporates the roasted concentrate and fluxes
- Other oxygen-containing lead materials such as oxides and silicates
- Metallurgical lump coke as the reducing and heating fuel

Process Description

The lead blast furnace is a countercurrent reactor in which a charge (sinter and coke) moves through a vertical shaft in countercurrent to the ascending gas flow. The descending charge successively passes through the preheating zone (to ca. 200 °C), the reaction or reduction zone (to ca. 900 °C), the melting zone (to ca. 1150 °C), and finally the combustion zone (tuyère zone). The liquid reaction products collect in the furnace crucible, which is located below the tuyère zone.

Principles. In the combustion zone, atmospheric oxygen blown in through the tuyères reacts with the coke to form carbon dioxide with extensive release of heat. This hot gas ascends through a coke-rich layer (arch) and is reduced to carbon monoxide, the main reductant. In the melting zone and in the overlying reduction zone, heat is transferred from the gas and liquid slag is formed from the fluxes and sinter gangue. Most of the metal-forming reactions take place in the softening-melting

zone, even though the residence time in this zone is relatively short. Before fusion, heterogeneous gas-solid reactions and heat transfer processes take place. Free moisture and water of crystallization are driven off in the preheating zone.

The rates of coke combustion and conversion of carbon dioxide to carbon monoxide (Boudouard reaction equilibrium) must be in accordance with the rate of reduction in the reaction zone and with the rate of heat transfer. If the combustion rate exceeds the rate of heat transfer to the charge, the coke burns more rapidly than the charge melts causing the melting zone to rise in the furnace. If the combustion rate is lower than the rate of heat transfer, the coke burns so slowly that it prevents the charge from descending and slows down the performance of the furnace. If the rates of combustion and heat transport are in good agreement, the melting zone and thus the plastic region are narrow. The charge material then flows through at a uniform speed and gas channeling and blow holes are minimized.

For optimal heat and mass transport in the reaction zone, gas velocity should be high and the resistance to gas flow low. The physical and chemical characteristics of the sinter should ensure adequate solids integrity in the reaction zone. Finally, the blast furnace charge should be as physically homogeneous as possible.

Behavior of Sinter Components. The exothermic reduction of lead oxide by carbon, carbon monoxide, and hydrogen begins at relatively low temperature. Other oxygen-containing lead species (e.g., aluminates, silicates, and ferrites) require more intense reducing conditions. Lead sulfate and the basic lead sulfates are converted chiefly by reaction with silicates, but they can also react with sulfides to yield metallic lead. Lead sulfide partly reacts with sulfates to form metallic lead.

The noble metals are largely dissolved in the lead product (*bullion*), with small amounts distributed to sulfide matte and slag.

The copper content of the sinter is captured in the matte in sulfide form, provided suffi-

cient sulfur is present. If, however, the sulfur level is insufficient, the copper is reduced and goes into solution in the lead bullion. A small portion of the copper is always incorporated into the slag in either oxide or sulfide form.

Zinc oxide is located in the slag, and to keep it in solution the slag must be rich in iron(II) oxide. Zinc levels in slag exceeding 18–20% cause slag viscosity problems and some hearth accretions. Part of the zinc oxide is reduced to zinc vapor above the tuyère zone, but the vapor is immediately reoxidized to zinc oxide in the colder zone (zinc circulation in the blast furnace). Zinc sulfide, charged in the sinter or formed from metallic zinc, is notorious because it promotes the formation of accretions on the walls of the smelting shaft. If a matte is formed, it can dissolve a certain amount of the zinc sulfide, but then its melting point rises and the physical separation of the slag becomes more difficult.

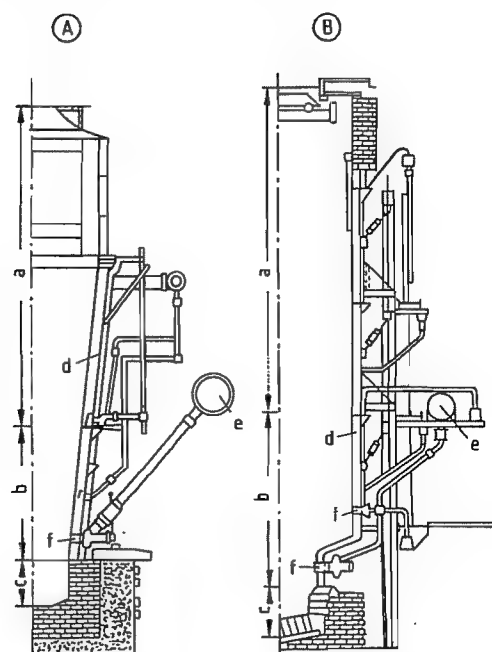


Figure 9.5: Blast furnace profiles. A) Single-level tuyère furnace; B) Double-level tuyère furnace. a) Upper shaft (preheating); b) Lower shaft (melting, reduction, tuyère zone); c) Crucible (slag, lead); d) Shaft and tuyère water jackets; e) Blast air bustle pipe; f) Blast tuyères.

Antimony and arsenic compounds are reduced to the respective metals which dissolve in the lead bullion. If the amount of arsenic is too large to be absorbed by the matte, and if copper, iron, and nickel are also present, metal arsenides (*speisses*) may be formed. Some arsenic is also volatilized and some is slagged. Tin is partly reduced into the lead bullion.

Separation of the fused products leaving the furnace hearth is based on their low mutual solubility and their differing densities (lead bullion about 10.5, matte 4.5–5.0, slag 3.5–3.8 g/cm³).

Lead Blast Furnaces

Lead blast furnaces are classed in two groups: round (*mushroom furnaces*) and rectangular (*Rachette furnaces*). The round design is only used in special low-capacity operations. The Rachette furnace is the standard type of lead blast furnace, and often has rounded corners. The *chair-jacket furnace* is a modification of the Rachette design and has two rows of tuyères, one above the other. Figure 9.5 shows two conventional blast-furnace profiles.

A typical lead blast furnace has a rectangular cross section 5–8.5 m above the tuyères, a water-cooled melting zone, and a syphon tapper for continuous lead discharge. For a given charge, furnace capacity can be increased only by enlarging the cross section. The area of the tuyère zone is the controlling factor. The world's largest furnace, employed by the Broken Hill Associated Smelters, Port Pirie, Australia, has a tuyère zone length of 10 m. Structural and operating data for this furnace are listed below:

Number of furnaces	1
Type	Rachette type with chair jackets
Furnace feed	
sinter, t/d	1250
total, t/d	1415
coke as % of sinter	9.5
Bullion production, t/d	550
Blast air	
rate, m ³ /min	510
pressure, kPa	120
Hearth area, lower, m ²	17.13

upper, m ²	30.34
Number of tuyères	
sides	81
ends	10
Tuyère diameter, mm	122
Nozzle diameter, mm	65
Elevation of bottom tuyères above hearth, mm	742
Furnace coke	
fixed carbon, %	82
carbon combustion rate, t m ⁻² d ⁻¹	3.3
Top gases, m ³ m ⁻² min ⁻¹ (STP)	16.2
Type of lead tapper	Asarco-Roy

The tuyère zone width can be increased only as long as the blast can penetrate from both sides, generally to around 1.5 m. The furnace can be widened if two offset rows of tuyères are placed one above the other such that the center ("dead zone") of the charge is brought to the melting point in the narrower bottom tuyère zone. Since the penetration depth of the blast in the furnace permits a maximum width of 1.8 m in the bottom tuyère zone, the top tuyère zone has a maximum width of 3.6 m. Widths of 1.5 and 3 m have been achieved in practice. The cooling jackets have the shape of a chair, which gives this configuration its name (Figure 9.5B).

The furnace shaft was formerly constructed of refractory bricks, but in modern furnaces a series of supported water jackets form the shaft, which may be either vertical (Figure 9.5B) or taper toward the bottom (Figure 9.5A). The hearth is subjected to the highest temperature and is cooled by one or more rows of replaceable cooling jackets set one on top of another.

The jackets are cooled with water that is either pumped in a closed cycle or circulated by the thermosiphon principle (i.e., natural convection). Jacket cooling by evaporative cooling (steam generation) is practised in the former Soviet Union. The water jackets have openings for the tuyères through which the blast enters. Combustion air must be at a pressure between 5 and 20 kPa. The resistance of the furnace depends not only on the quantity of blast injected but also on the permeability of the charge. Blowers whose delivery is valuable but independent of the furnace back-pressure are most suitable. These requirements are best met by positive blowers with a variable

speed, but equipment wear often dictates their replacement by centrifugal blowers.

Tests at several lead smelters have demonstrated that enrichment of the blast with oxygen increases throughput (ca. 5% increase for each additional 1% oxygen in the blast). When oxygen replaces part of the blast air, a higher combustion zone temperature is achieved, gas flow per unit of lead is reduced, and the furnace operates more smoothly. Benefits include increased production, a reduction in coke consumption, lower off-gas temperatures, and lower dust generation. Similar results have been achieved with preheated blast air. Whether oxygen enrichment or blast preheating is preferable depends only on economics. Oxygen enrichment has become more popular, especially since low-cost oxygen production has become increasingly common. However, as yet the degree of enrichment of the lead furnace blast is very modest: only 2–3%.

A crucible located below the tuyères serves to separate the liquid products and collect the lead. In large production units, lead is withdrawn continuously, and in smaller ones tapped at intervals. If the lead bullion has a high copper content, the continuous syphon tapper runs into accretion problems. It should be replaced by a discontinuous tapper placed just above the bottom of the crucible, so that it is always covered with molten lead to protect it against deposits. With the Asarco (Roy) continuous tapper the liquid phases are separated outside the furnace [10]. Lead and slag are discharged together into an external settler attached to the furnace, in which the liquid phases are separated. The Asarco tapper gives higher capacities with lower investment and maintenance costs, along with more hygienic workplace conditions. It has the drawback of a higher lead level in the slag. North American smelters employ the Asarco tapper; some European smelters use the Arents syphon tapper.

If a separate matte phase is formed, slag and matte can be separated in a heated launder, where the matte with its higher relative density settles and the slag floats. If the slag is to be discarded or kilned for zinc recovery, it is

usually granulated. It may, however, also be transported in the molten state to a zinc fuming furnace.

The charging of blast furnaces is largely automated. Charging devices for open-top furnaces may be bucket elevators and skips or a variable discharge conveyor belt. Tipping or bottom dump charge buckets are used for the more common closed-top furnaces. Various alternating charging techniques are employed to achieve layers or blends of coke and sinter in the shaft. Blast-furnace top gases are drawn off the furnace top by an exhaust fan and passed through a baghouse for dust removal.

Products of the Lead Blast Furnace

The lead blast furnace yields the following products:

- **Lead bullion**, which must be further refined.
- **Slag**, which may contain large amounts of zinc and must then be further processed.
- **Flue dusts and baghouse dusts**, which consist of fumes and dust particles carried over by the furnace top gases. Cadmium tends to accumulate in this dust, and sometimes a special cadmium separation leach is carried out before the dust is recycled to sintering.
- **Top gas**. Blast furnace top gas usually contains 3–4% carbon monoxide, which represents an unavoidable energy loss. With normal heat exchange between gas and solids in the shaft the top gas is too cold for practical heat recovery, so after dust removal it is released to atmosphere.
- **Matte**, a sulfidic product of blast-furnace smelting, forms only if the burden contains enough sulfur. In general, provided the charge does not contain too much copper or sulfur, matte phase formation is avoided with the copper remaining in solution in the lead bullion and slag. Subsequent reverberatory melting of lead bullion drosses yields copper matte, lead metal, and slag. The copper matte can contain varying amounts of lead, iron, zinc, and noble metals. Copper matte is usually sold to special copper smelters, but processing of matte to copper

sulfate or copper metal is becoming more common.

- **Speiss** is only formed when the burden contains amounts of arsenic, nickel, cobalt, and antimony that are so large that they can no longer be taken up by the matte. Speiss is undesirable, because it dissolves large quantities of noble metals and also requires expensive refining.

Composition and Processing of Slag. The slag consists of gangue, fluxes, and the zinc contained in the charge. It also contains dissolved and suspended metals (lead, copper, silver), which are a potential economic loss. The chemical and physical properties of the slag have a considerable effect on furnace throughput, product separation, metal recovery, and coke consumption in the furnace. Lead blast furnace slag should have a low melting point, be adequately fluid (low viscosity) at the furnace bottom temperature [11], and have minimal density. Slags are compounded to attain these properties by fluxing to selected component ratios. Thus, in the ternary system CaO-FeO-SiO_2 almost all lead blast furnace slag compositions lie in an area that is bounded by weight ratios of 1:1 to 4:1 for $\text{SiO}_2:\text{CaO}$ and 1:2 to 3:2 for $\text{SiO}_2:\text{FeO}$ (Figure 9.6). This is further illustrated in Figure 9.7 for a number of North American and Australian lead blast furnaces.

Lead blast-furnace slag often contains sufficient zinc to make recovery profitable by rotary kiln or submerged combustion slag fuming. In both cases zinc oxide in the slag is reduced to metallic zinc (vapor) by carbon, oxidized by secondary air, and carried out in the furnace gases for recovery of zinc oxide dust.

Zinc recovery rotary kilns (Waelz kilns) are up to 95 m long with an internal diameter of up to 4.5 m and they are lined with refractory material. The granulated blast-furnace slag is mixed with other zinc intermediates (steel dusts, etc.) and solid fuel reductant; it travels down the kiln and is heated to reaction temperature by combustion gases from a burner at the discharge end. The stripped slag is usually

close to its melting point at discharge, and normally contains 2–3% zinc and < 0.25% lead. Production from a Waelz kiln is about 120–155 kg of zinc per day per cubic meter of furnace volume, declining with increasing furnace size. The captured dust contains roughly 75% zinc and lead. Zinc recovery is 88–95% and lead recovery is about 90–98%.

In the *slag-fuming process* a mixture of coal dust and air is injected through tuyères into a liquid blast-furnace slag at 1150–1250 °C in a water-jacketed furnace. The slag is delivered in liquid form directly from the lead blast furnace and may have up to 30% of solid granulated slag or slag skulls added to it. The process is typically operated in batch mode in furnaces of 50–100 t capacity.

At the Plovdiv lead smelter in Bulgaria, slag is tapped continuously from the lead blast furnace through a slag syphon. It then flows through a preheating electric furnace (+ 100 °C) and enters the continuous slag fuming furnace. Heavy fuel oil is used as reductant

rather than the more conventional pulverized coal.

Metal recoveries in slag fuming plants are about the same as in Waelz kilns. Slag fuming furnaces normally recover heat from the hot gases in waste heat boilers or air heat exchangers.

Imperial Smelting Process

In the Imperial Smelting process, lead and zinc are produced together in a single blast furnace operation. This is basically a zinc production process in which lead is also obtained. It is especially well-suited to processing lead-zinc mixed concentrates. The zinc to lead ratio in the sinter mixture is usually 2:1. The furnace design is similar to that of conventional lead blast furnaces of the chair-jacket type, but there is only one row of tuyères. The top is closed by a double-bell system. For process principles and description, see Chapter 10.

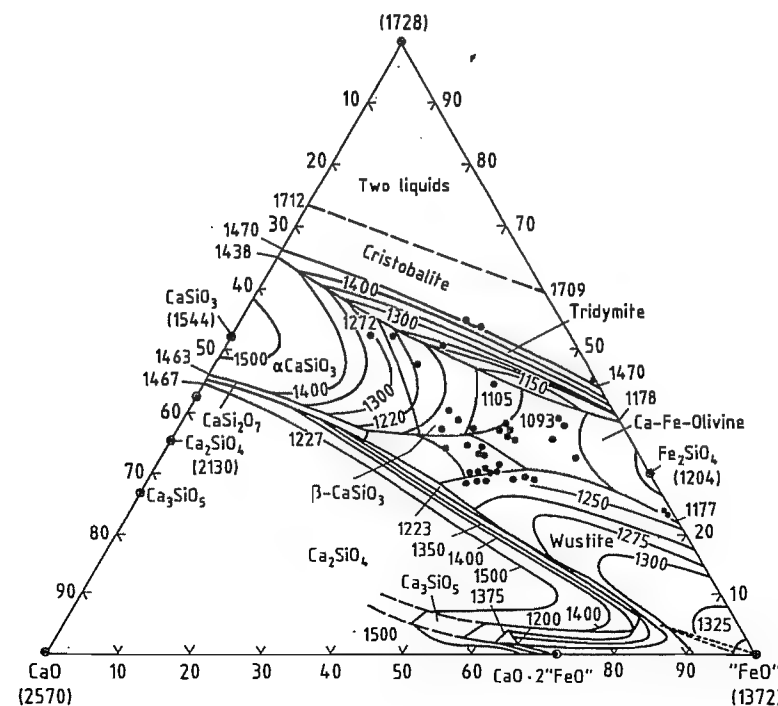


Figure 9.6: The $\text{FeO-SiO}_2\text{-CaO}$ ternary system, showing compositions of several lead blast furnace slags (•) [12].

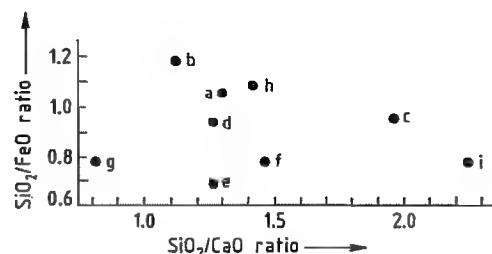
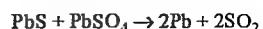
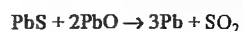


Figure 9.7: SiO₂:FeO and SiO₂:CaO weight percentage ratios in blast furnace slags [13]: a) Asarco, East Helena; b) Asarco, El Paso; c) Asarco Glover; d) Amax; e) Brunswick M&S; f) Cominco; g) Mount Isa; h) BHAS, Port Pine; i) St. Joe Lead.

9.5.3 Roast Reaction Processes

Lead sulfide reacts with lead oxide or lead sulfate to form metallic lead and sulfur dioxide in the roast reaction:



A number of processes dating from the earliest times have been used to recover lead by partial air oxidation of lead sulfide. These processes are categorized as excess sulfur or excess oxygen, depending on whether the reaction series exhausts the oxide and sulfate or the sulfide species, respectively. High-grade lead concentrates are required in order to maximize the activities of the lead species and, therefore, lead recovery.

The principal commercial example of the excess sulfur type is the *Boliden electric furnace process*. Since this process contains elements of flash smelting, it is described in Section 9.5.4.

An example of the excess oxygen roast reaction chemistry is the *Scotch (Newnham) hearth process*, one of the earliest lead-making techniques. The old furnace design was improved and automated in the Bleiberg Bergwerks Union (Schlippenbach) rotary hearth [14]. This process produces a small quantity of high-lead (grey) slag which requires separate recovery treatment, and low-strength sulfur dioxide gas, unsuitable for production of sulfuric acid. The hearth processes

are now antiquated and are responsible for a very small amount of lead production.

9.5.4 Direct Smelting Reduction Processes

The fundamental problems encountered in the sinter, oxidation-blast furnace method of lead production (e.g., high process and hygiene ventilation gas volumes, high maintenance costs for sintering machinery, and expensive coke fuel for reduction) have long been recognized. The quest for a simpler, more direct smelting system has been pursued for many years, and several new processes have now achieved industrial application.

Table 9.2 summarizes the key features of the most prominent new lead smelting processes. They can be classified into two principal categories: *flash smelting* of dried feed mixtures using air or oxygen, and *bath smelting* of undried feed mixtures also with air or oxygen. Oxidation of the feed produces a medium-strength sulfur dioxide gas, a variable amount of lead bullion, a slag rich in lead monoxide, and a lead sulfate flue dust which must be recirculated.

The strength of the sulfur dioxide gas produced depends on the degree of oxygen enrichment and the amount of auxiliary fuel required for autogenous operation of the oxidation step. With the use of oxygen, sulfur dioxide gas contents of 20–30% are typical.

The amount of direct-smelt lead bullion produced during the oxidation step depends on the thermal balance. In the case of direct smelting of a very high-grade lead concentrate, up to 80% of the lead in the charge can be obtained as direct bullion with the remaining 20% as a slag rich in lead monoxide. With low-grade feed charges requiring auxiliary fuel, all lead can be oxidized to a high-lead slag, with no direct bullion production.

The second step in direct smelting processes is reduction of lead from the high-lead slag (25–40% Pb). Slag has been successfully reduced by submerged fuel combustion or injection, reduction assisted by an electric furnace, and a combination of these techniques.

Table 9.2: Summary of direct smelting lead processes.

Process	Smelting type	Source of oxygen	Special features
Boliden Electric furnace	dry charge flash smelting continuous	enriched air	flash oxidation in freeboard of electric furnace; slag reduction by coke breeze in electric furnace; lead bullion is high in sulfur requiring special treatment
Kivcet	dry charge flash smelting continuous	technical oxygen	an electric furnace freeboard is separated into an oxidation flash smelting shaft and a slag reduction section by a partition wall extending into the slag bath; majority of slag reduction is done by coke checker at bottom of smelting shaft
Boliden Kaldo	batch dry charge flash smelting into TBRC vessel	technical oxygen	batch oxidation is followed by slag reduction in same vessel using PbS followed by coke reductant
Outokumpu	dry charge flash smelting continuous	technical oxygen	slag reduction done in separate electric furnace employing powdered coal injection with nitrogen through lance
Isasmelt	moist charge slag bath smelting continuous	air or enriched air	air is injected into slag batch by Siros melt lance; feed dropped into slag bath; slag reduction by coal in a similar lance-vessel unit
QSL	moist charge slag bath smelting continuous	technical oxygen	horizontal cylindrical reactor divided into oxidation and reduction sections by refractory wall; oxygen injected into lead-slag bath through nitrogen shrouded tuyères; moist feed dropped into slag bath; slag reduction by submerged combustion of oxygen fuel in gas shrouded tuyères

9.5.4.1 Air Flash Smelting

Boliden Process [15]. Dry, high-grade galena concentrate (65–75% Pb) is blown into an electric furnace with oxygen-enriched air. Limestone flux and coke breeze are also included in the feed charge. Suspended lead sulfide particles react to produce lead monoxide and lead metal, which collect in the furnace hearth along with the fused slag constituents. Desulfurization is not complete. The furnace products are lead bullion containing 2–3% sulfur, slag containing 4–5% lead, and flue dust. Desulfurization of bullion is completed by air blowing in a downstream converter.

The Boliden electric furnace process has operated successfully since 1963 at the Rönnskär Smelter in Skelleftehamn, Sweden. The 8000-kVA smelting furnace employs four Söderberg electrodes. Product slag is treated in a slag fuming furnace along with copper slag for zinc and lead recovery. A section of the electric furnace is shown in Figure 9.8 and typical daily furnace charge and production figures are listed below:

Charge	
concentrate	280 t
limestone	40 t
iron oxide	7 t
coke breeze	7 t
recycle flue dust	140 t

drosses	15 t
oxygen enrichment	25% O ₂
Products	
slag	70 t (34% CaO, 17% Zn)
bullion	280 t

Several drawbacks have prevented wider industrial application — high-grade lead concentrate is required, flue dust production is high, and bullion treatment is required to remove residual sulfur.

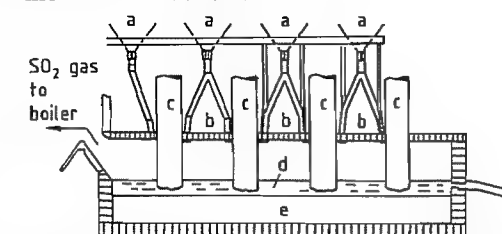


Figure 9.8: Boliden lead smelting electric furnace: a) Dryfeed hoppers; b) Dry feed-air injection ports; c) Söderberg electrodes; d) Slag bath; e) Lead bullion.

9.5.4.2 Oxygen Flash Smelting

The most prominent oxygen flash smelting processes for lead production are the Kivcet CS process developed in the former Soviet Union [16], the Kaldo process developed by Boliden in Sweden [17], and the Outokumpu process developed in Finland [18]. In all these processes, very complete desulfurization of

the charge is effected through the production of a strongly oxidizing slag. The required oxygen potential can only be achieved with lead monoxide when its weight fraction is high (> 35% lead in the initial slag) [19]. The other major slag components are in ratios very similar to those found in blast-furnace slag.

Kivcet Process

The Kivcet process was developed at the Vniitvetmet Institute, Ust Kamenogorsk, former Soviet Union. Of the recently developed smelting processes, the Kivcet process is the most advanced, with industrial plants operating at the Ust Kamenogorsk Lead-Zinc Combine and at the Samim lead-zinc metallurgical complex in Portovesme, Sardinia. The Kivcet furnace at the Samim plant is a sophisticated structure, employing extensive water-cooling on the furnace side walls and in the smelting shaft. The general process flows are shown in Figure 9.9. Figure 9.10 shows a section of the smelting furnace at Portovesme.

As shown in Figure 9.10, the oxidation section of the electric furnace freeboard is separated from the reduction section by a water-cooled, gastight wall (d) which dips into the furnace slag bath. Dried and blended charge components consisting of lead concentrate and other lead-bearing materials, required fluxes, recycle flue dust, and oxygen are fed through burners (a) at the top of the oxidation shaft (b). Combustion of charge constituents at a temperature up to 1400 °C and a shaft height of 3–5 m permits almost complete desulfurization before collection of the reaction products in the slag bath (f).

Reduction of the lead monoxide from charge combustion is accomplished mainly by using a layer of coke particles floating on the slag bath under the submerged partition wall (d) into the reduction section of the electric furnace where reduction of lead monoxide is

completed to produce a slag containing 2–3% lead. If desired, additional coke breeze reductant and electrical energy can be used to fume zinc. In this mode of operation, product slag containing 3–4% zinc and 1–2% lead can be obtained. Zinc fumed in the electric furnace can theoretically be recovered as metal using a lead splash condenser, but a simpler approach is to burn the zinc vapor to zinc oxide in a combustion flue (h) and recover an oxidized flue dust for further zinc recovery processing.

Lead bullion is removed from the furnace by a syphon and slag is withdrawn continuously from a weir overflow.

Sulfur dioxide gas from the combustion shaft passes under a water-cooled partition wall before rising in an extended vertical wall boiler duct. Cooling of the sulfur dioxide gas flue dust mixture to 450 °C is accomplished in the vertical boiler stack (e) before the gases enter an electrostatic precipitator for separation of the lead sulfate fumes. Flue dust production is moderate, about 10–20% of the feed charge weight.

The Kivcet process can smelt oxidic charge materials such as zinc leach residues. Extra auxiliary fuel for adequate flame temperature and sufficient shaft height for adequate retention time must be provided to achieve the required degree of desulfurization.

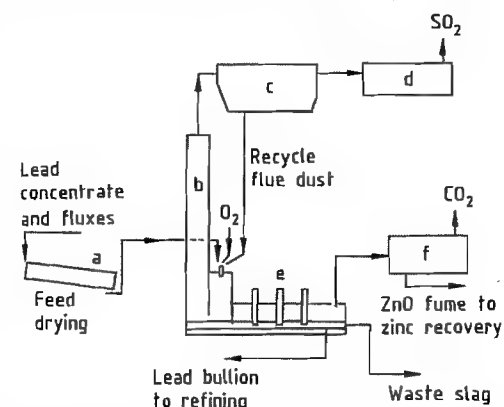


Figure 9.9: Kivcet lead smelting process: a) Feed drying; b) SO₂ gas cooler; c) SO₂ gas cleaning electrostatic precipitator; d) SO₂ gas scrubber; e) Flash smelting furnace; f) Electric furnace gas cleaning.

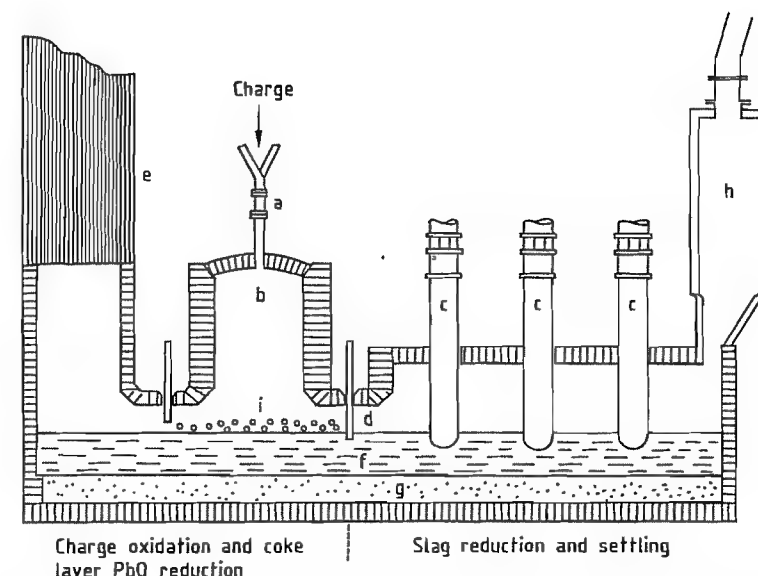


Figure 9.10: Kivcet lead smelting furnace (Portovesme, Italy): a) Oxygen burner for dry feed; b) Flash smelting shaft; c) Furnace electrodes; d) Partition wall; e) Membrane wall SO₂ gas cooler; f) Slag bath; g) Lead bullion; h) Zinc fume combustor-cooler; i) PbO reduction coke layer.

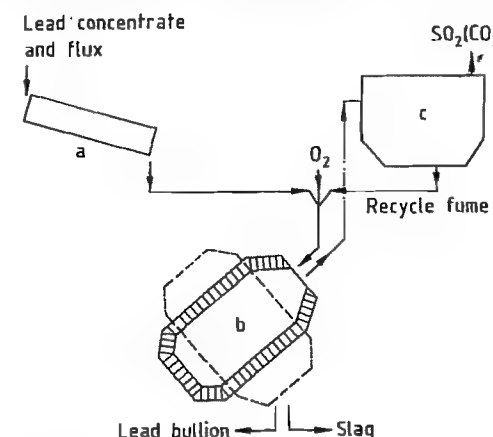


Figure 9.11: Boliden Kaldor process: a) Feed drying; b) Kaldor vessel; c) Gas cooling and cleaning.

Boliden Kaldor Process

The Boliden Kaldor process employs a top-blown rotary converter in a batch manner. A cycle starts with oxygen combustion of dry charge constituents into a preheated empty vessel. Figure 9.11 shows the process flows. Charge combustion is continued until lead

bullion and high-lead slag have accumulated to the limit of vessel weight or volume capacity. Charge combustion is then stopped and slag reduction commences. Lead sulfide concentrate is used to reduce a major portion of the lead monoxide in the slag, followed by coke breeze reduction to discharge slag composition. The vessel's slag and bullion contents are then poured into ladles, and the smelting cycle repeated.

The Boliden Kaldor process can handle a variety of lead-containing charge materials such as secondary scrap and flue dusts. The cyclic production of sulfur dioxide bearing gas and barren reduction gas introduces some complications to the gas handling and sulfur dioxide recovery system.

Outokumpu Process

Outokumpu Oy of Finland pioneered the air flash smelting of copper concentrates in the late 1940s, and this process has become standard worldwide. Experimental work on air flash smelting of lead concentrate in pilot plants was carried out in the 1960s. Little

commercial interest was shown at that time, and pilot-plant testing on several types of lead concentrates was not resumed until the late 1970s, when oxygen rather than air was used for the flash smelt. Full-scale lead smelter engineering studies have been carried out, but to date no production plants have been constructed.

The process scheme of the Outokumpu lead flash smelting process is shown in Figure 9.12. Lead concentrate and flux are dried in a rotary dryer (a), mixed with recycle flue dust, and then flash smelted with oxygen in the oxidation furnace smelting shaft (b). High-lead slag and lead bullion collected in the furnace hearth may be tapped separately to provide a direct lead bullion product. Alternatively, if direct lead bullion production is small, slag and bullion are tapped together into a separate electric slag reduction furnace (d). In the electric furnace, pulverized coal is injected with nitrogen into the slag bath to reduce lead monoxide.

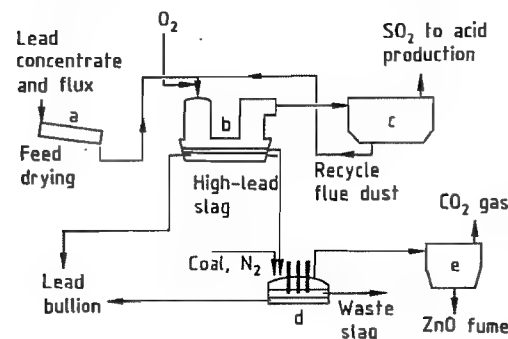


Figure 9.12: Outokumpu lead smelting process: a) Feed drying; b) Flash smelting furnace; c) SO_2 gas cooling and cleaning; d) Electric slag reduction furnace; e) Electric furnace gas cleaning.

The pilot-plant equipment consisted of a rotary dryer, dry concentrate bins, pneumatic conveyors for concentrate and recycle flue dust, a flash furnace (15 m^3), a waste heat boiler (3 t/h steam), an electrostatic precipitator, and a 2 MVA electric furnace.

The pilot plant processed 3–5 t/h of concentrate ranging from 47% to 75% lead content. Bullion and slag were continuously tapped to

the electric furnace for slag reduction. About 10 000 t of lead concentrate were processed.

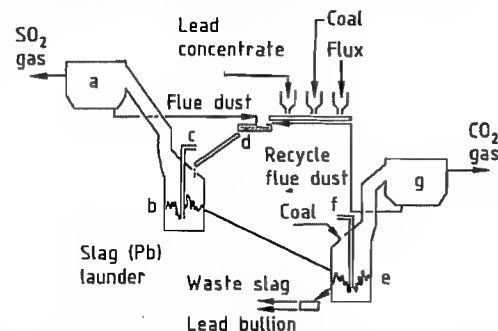


Figure 9.13: Isasmelt lead process: a) SO_2 cooling and cleaning; b) Oxidation; c) Lance for oil and air; d) Feed mixing; e) Reduction furnace; f) Lance for oil and air; g) Reduction gas cooling and cleaning.

9.5.4.3 Air-Slag Bath Smelting, the Isasmelt Process

The Isasmelt process (Figure 9.13) consists of two stages and was developed by Mount Isa Mines and Csiro in Australia [20]. Both stages, the charge oxidation stage and the slag reduction stage, employ a stationary, cylindrical, refractory-lined reaction vessel. The process features the Sirosmelt lance, which is a steel pipe that is cooled by the high-velocity process air which it injects into the melt. In the oxidation vessel (b), air or oxygen-enriched air and supplementary oil fuel are injected through a Sirosmelt lance (c) into the center of the vessel. The blended feed materials (d), lead concentrate, fluxes, and moist recycle flue dust are dropped into the slag bath and agitated by the lance burner. Virtually all the charge lead content is oxidized to a high-lead monoxide slag. The slag is transferred to the reduction vessel (e), which employs a similar air fuel lance (f), with additional lump coal charged separately as reductant.

Starting in 1983, a 5 t/h concentrate feed demonstration plant was used to prove the smelting stage of the process. In the first year of operation, 21 000 t of lead concentrate were treated to produce high-lead monoxide slag, which was subsequently processed by sintering and blast furnace reduction. In 1985, con-

struction of the second-stage reduction vessel demonstration plant was started. At the present time the installation of a full-scale production plant at Mount Isa is being studied.

A cross-section of the oxidation furnace is shown in Figure 9.13 (b). The furnace consists of a cylindrical steel shell, 2.7 m in diameter and 4.5 m high, lined with chrome magnesite bricks backed with an insulation lining. Typical analyses are given in Table 9.3. Operating conditions for the demonstration plant are as follows:

Lead concentrate rate	4 t/h
Smelting temperature	1030 °C
Air: concentrate ratio	125 % of theoretical
Fume rate	10 % of lead in feed
Flux addition	12 % of concentrate rate
Oil requirement	25 kg per tonne of concentrate

Table 9.3: Typical analyses from the Isasmelt demonstration plant oxidation vessel.

Component	Lead concentrate, %	Slag product, %
Pb	47.3	51.8
Zn	7.0	7.6
Fe	12.4	13.6
SiO_2	2.8	9.8
CaO	0.9	1.5
S	23.8	0.3

9.5.4.4 Oxygen-Slag Bath Smelting, QSL Process

The QSL Process is named after its inventors, P. E. QUENEAU and R. SCHUHMAN JR., as well as the process developers Lurgi Chemie [21]. Development of the process progressed through bench-scale tests in 1974–1975, pilot-plant operation in 1976–1979, and a demonstration plant operation at Metallhüttenwerke, Berzelius, Duisburg, Germany from 1981 to 1985. Three commercial plants were constructed: in Trail, Canada (Cominco Ltd.), in Germany (Berzelius Binsfeldhammer Smelter), and in China. The Canadian plant was shut down and dismantled after a brief operation.

Figure 9.14 shows the general scheme of a QSL process lead smelter. Lead concentrate, fluxes, auxiliary coal fuel, recycle flue dust, and other charge components are blended (b) in a moist condition to form a single feed

charge to the QSL reactor. The reaction vessel is a horizontal refractory-lined cylinder that is divided by a partition wall into an oxidation section (c) and a slag reduction section (d). The working dimensions of the demonstration plant reactor (10 t concentrate per hour, 30 000 t of lead per year) were 2.5 m (diameter) by 22 m (length, 7 m of which is occupied by the oxidation zone). Nitrogen-shrouded tuyères on the bottom of the reactor injected oxygen into the oxidation section. Similar shrouded tuyères were employed for submerged combustion of oxygen-coal or oxygen-natural gas reduction mixtures. Blended feed was charged through ports at the top of the oxidation reaction section into the injection-agitated lead and slag bath.

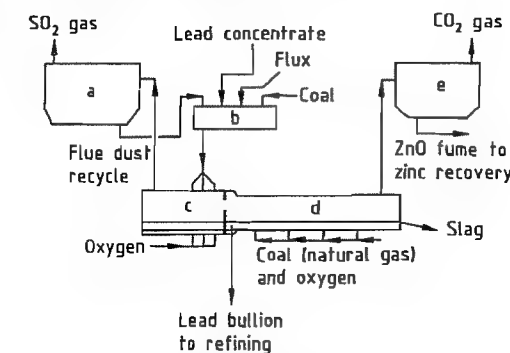


Figure 9.14: QSL lead smelting process: a) Oxidation gas cooling and cleaning; b) Feed mixing; c) Oxidation section; d) Slag reduction section; e) Reduction gas cooling and cleaning.

The oxidation products in the QSL process are high-lead slag, sulfur dioxide gas, flue dust, and lead bullion. The amount of lead produced in the oxidation zone depends on the charge makeup and lead concentrate grade. Slag from the oxidation zone flows through an underflow port in the vessel partition wall into the slag reduction zone (d). Lead bullion is removed by a lead syphon at the side of the vessel. The smelting vessel is rotated by 90° during stoppages to bring the injection tuyère systems above the vessel slag level. Inspection of the refractory and tuyère maintenance can be carried out with the vessel in this standby position.

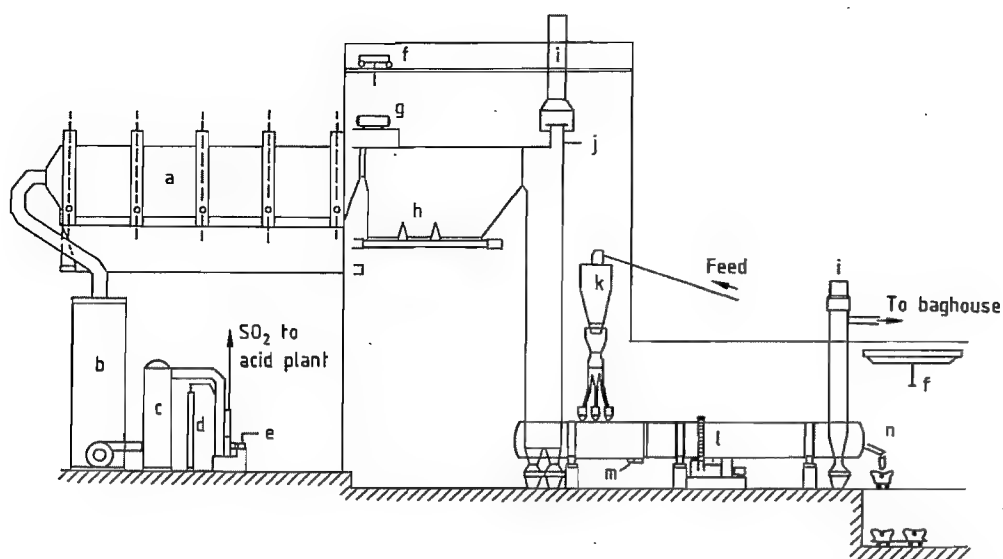


Figure 9.15: QSL lead smelting plant (Trail, Canada): a) Electrostatic precipitator; b) Spray tower; c) Cooling tower; d) Stripper; e) SO₂ fan; f) Crane; g) Steam drum; h) Waste heat boiler; i) Emergency stack; j) Cooling channel; k) Feed bin; l) Reactor; m) Lead syphon; n) Slag tap.

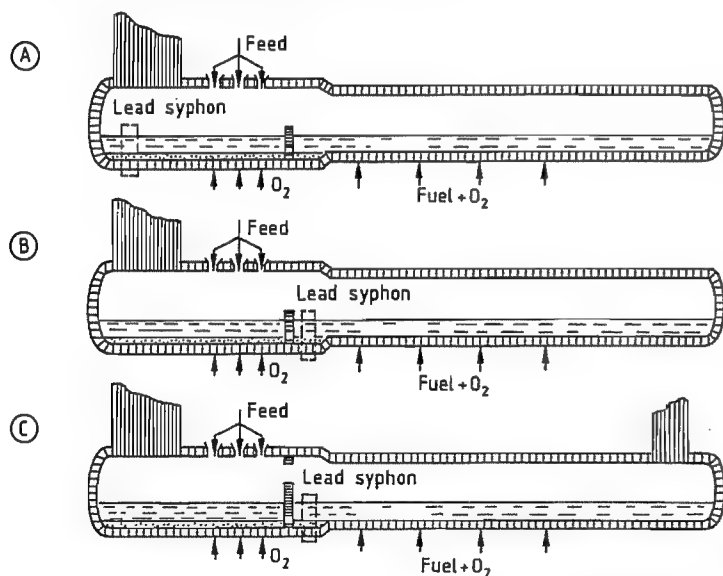


Figure 9.16: QSL smelting vessel configurations. A) Conventional, low arsenic-antimony bullion; B) Increased arsenic-antimony recovery in bullion; C) Recovery of zinc oxide fume.

Figure 9.15 shows the QSL smelting plant in Trail, Canada. The reaction vessel has dimensions of 4.5 m (diameter) by 12.5 m (length) in the oxidation section, and 4.0 m (diameter) by 28 m (length) in the reduction

section. Nominal plant capacity is 160 000 t/a of lead and 230 000 t/a of reduced slag. Reduction is performed with partially combusted natural gas. Three smelting vessel configuration options are shown in Figure 9.16.

Figure 9.16A. This is the simplest smelting configuration and is employed at the Duisburg demonstration plant. Reduction gas and oxidation gas flow into the same gas cooling system. Reduction and fuming of zinc in the reduction zone is controlled to limit zinc circulation in recycle flue dust. Lead bullion produced in the reduction zone flows countercurrent to oxidation slag through the partition wall underflow port. The product lead bullion is withdrawn from the oxidation end of the furnace. With this configuration the arsenic and antimony contents are minimized in the bullion and maximized in the reduced slag.

Figure 9.16B. This differs from the previous option in that the product bullion syphon is located on the reduction side of the slag partition wall. Arsenic and antimony in bullion are maximized with this option.

Figure 9.16C. This smelting vessel configuration has an auxiliary gas offtake at the reduction end of the vessel for withdrawing a zinc-bearing reduction fume. The lead syphon is located on the reduction side of the partition wall for maximum arsenic and antimony deportment to bullion. This design is employed in the Cominco Trail smelter.

9.5.5 Other Lead Processes

Several other lead processes have been tested on small and pilot scales but none has been commercialized. The *Halkyn process* involves the fused-salt electrolysis of lead sulfide dissolved in molten lead chloride; it has been modified and improved, most recently by the U.S. Bureau of Mines [22]. Trouble-free fused-salt electrolysis is feasible only with high-quality lead concentrates; high contents of impurities (e.g., copper) cause the formation of barrier layers and cell complications.

Wet processes have not succeeded although many have been investigated in the chloride, nitrate, sulfate systems, and with selective alkylamine leaching of lead sulfate followed by carbonation of lead. An alternate leaching system employs ammoniacal ammonium sul-

fate, which also dissolves lead sulfate well and is cheaper than the amine solutions.

9.6 Refining of Lead Bullion

Production lead, known as bullion, contains numerous dissolved impurities. Molten lead is an excellent solvent for a variety of metals and compounds, and raw bullion commonly contains copper, iron, zinc, sulfur, arsenic, tin, antimony, bismuth, noble metals (silver, gold, platinum group metals), oxygen, and occasionally nickel, cobalt, and tellurium. The lead content varies between about 90 and 99.9% depending on the process and feed quality. The percentages of impurity contents for blast-furnace lead bullion treated in refining plants are as follows:

Cu	0.2–4.0
Fe	0–0.5
Zn	0–0.5
Ni	0–0.1
Co	0–0.1
Co	0–0.1
As	0–2.0
Sb	0–6.0 (usually < 2.0)
Ag	0–2.0
Bi	0–6.0 (usually < 2.0)
Sn	0–4.0 (usually < 1.0)
S	typically 0.2–0.3
O	typically 0.1

The object of lead bullion refining is to produce pure commercial lead metal and to separate the valuable impurity metals into their most valuable marketable form. The two main refining routes used are pyrometallurgical and electrolytic. The latter is generally reserved for higher levels of impurities (especially bismuth).

Pyrometallurgical processes are generally operated in a batch manner; however, continuous operation is being applied to many of the process steps. The advantage of pyrometallurgical refining lies in the consecutive selective recovery of impurity metals.

In *electrolytic refining*, all the impurities are concentrated in the anode slime and must be separated by a relatively complicated process. On the other hand, electrolysis yields lead that is very low in bismuth (< 10 g of bismuth per tonne of lead), which cannot be eco-

nomically produced by the pyrometallurgical route. Over 90% of installed capacity for lead-bullion refining worldwide is based on pyrometallurgical methods.

9.6.1 Pyrometallurgical Refining

Principles. When metals are refined pyrometallurgically, impurities dissolved in the parent metal are enriched in a phase that is insoluble (or sparingly insoluble) in the parent metal. Enrichment can be achieved by adding reagents, by controlling the pressure and temperature, or by a combination of both techniques. Methods are classified as chemical, precipitation, and distillation processes.

Attention to the kinetics of the unit operations involved in lead refining is of the utmost importance. Kinetic reactors can govern the degree of refining that is attainable when the system is far removed from the theoretical chemical or physical equilibrium. In other systems the chemical equilibrium is approached closely. A good review of the physical chemistry is given in [23].

Chemical Processes. A reagent added to the parent metal reacts with one or more impurities to form a compound that is insoluble in the parent metal. Occasionally, fluxes are also used, for example to cause oxides formed in the solid phase to go into a liquid slag. Reagents include oxygen (atmospheric oxygen or oxygen-evolving salts), sulfur, and chlorine. The refining step is then referred to as selective oxidation, sulfurization, or chlorination. Reagent selection is based on a comparison of the free energy of formation of the oxides, sulfides, or chlorides of the parent metal and of the impurities in question.

Precipitation Processes. Generally, impurities become less soluble in the host metal as the temperature falls, and can be rejected either directly from the melt (e.g., copper from the binary system copper-lead), or as a compound with the parent metal (e.g., iron as FeZn_3 from iron-zinc solutions). Alternatively, suitable reagents can form insoluble compounds that can be skimmed off (e.g., bismuth from lead-bismuth solutions after addi-

tion of calcium and magnesium); this is really a chemical process that involves the formation of insoluble intermetallic compounds.

Distillation Processes. Distillation processes are employed when a large difference in vapor pressure exists between the parent metal and the impurity (e.g., in the separation of residual zinc from lead bullion after Parkes desilvering).

Process Steps. All of the above processes are used in the pyrometallurgical refining of lead bullion. A typical pyrorefining scheme is as follows:

- **Removal of copper** is a two-stage operation. The first stage is primary decoppering by *drossing* (precipitation). The second is *selective sulfidizing* of copper by the Colcord process, which involves the addition of sulfur (a chemical process).
- **Removal of arsenic, tin, and antimony** by selective oxidation with injected air or with oxidizing agents such as sodium nitrate in a caustic slag (Harris process).
- **Removal of noble metals** is usually called desilvering or desilvering and involves intermetallic precipitation with zinc by the Parkes process.
- **Removal of zinc** remaining after desilvering is achieved by vacuum distillation.
- **Debismuthizing.** If required to meet refined lead specifications, bismuth is removed by precipitation with alkali metals and/or alkaline earth metals, for example with calcium and magnesium in the Kroll-Betterton process.
- **Removal of alkali metals and alkaline earth metals** remaining after debismuthizing is called final refining and is performed by selective oxidation with air under a salt slag cover.

9.6.1.1 Decoppering

Drossing (Liquation). Copper is soluble to several percent in hot lead bullion but to only 0.06% at the freezing point. When the lead cools, copper and other impurities precipitate as a lead-rich *copper dross*. This process is al-

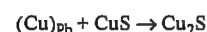
ways the first step in any lead refining operation. In the first phase of cooling to about 950 °C, nearly all dissolved iron and zinc are precipitated as oxides, magnetites, or spinels. The noble metals and other impurities with higher solubilities (e.g., copper, arsenic, antimony, tin, bismuth) remain dissolved in the lead.

In the next cooling stage, the copper compounds of sulfur, arsenic, antimony, and tin separate, along with considerable lead sulfide and entrained metallic lead. The large lead content must be separated by a dross retreatment process. Nickel and cobalt, if present, separate similarly to copper.

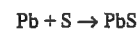
Fine decoppering may also be referred to as sulfur decoppering or sulfur drossing (Colcord process). After drossing, elemental sulfur is mixed into the molten lead bullion at the lowest possible temperature (320 °C) for selective sulfidization of copper. Lead(II) sulfide and copper(II) sulfide form stable phases in the ternary system Pb-Cu-S when liquid or gaseous sulfur is present. The copper sulfide can be produced by the reaction between copper-lead alloy and liquid or gaseous sulfur whenever there is a local excess of sulfur:



Copper(II) sulfide can decopper lead by the reaction



Sulfur simultaneously reacts with lead, but much more slowly than with copper:



The lead corner of the Pb-Cu-S system is shown in Figure 9.17 and suggests that the copper level can in theory only be decreased to about 0.05% by sulfur precipitation. With cooling, however, lead sulfide forms as well as copper(I) sulfide (Cu_2S). In fact copper levels of 0.001–0.002% can be achieved if minor amounts of silver or tin are also present and attention is paid to good shear stirring and gradual addition of sulfur [23]. This is because silver and tin slow down the reaction between lead and sulfur. Without silver or tin, 0.01% copper can be attained only by repeated sulfur

additions and with prohibitive sulfiding of lead.

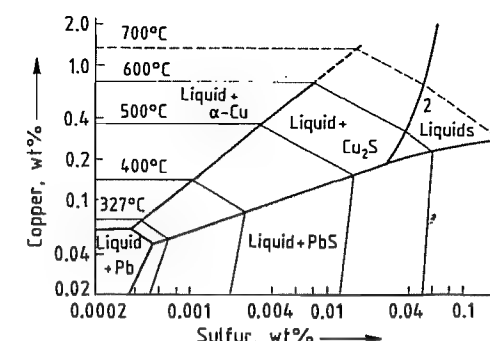


Figure 9.17: Lead corner of the Pb-Cu-S ternary system [23].

Process Engineering. Decoppering of lead bullion usually takes place immediately after the bullion is discharged from the blast furnace. In batch decoppering, drossing is carried out in kettles with capacities of up to 300 t. Powerful stirrers help separate the phases, allowing the formation of a "dry" dross containing little entrained lead metal. The dry dross is removed from the melt surface by skimming, usually with mechanically or pneumatically driven perforated scoops, or by suction. In industrial drossing, final copper contents of 0.06–0.12% are reached. This level of copper would greatly increase the zinc requirement for Parkes process desilvering, and therefore fine (sulfur) decoppering is always necessary.

An important advance is *continuous decoppering*, which combines decoppering and reprocessing of the copper dross in a single stage. Continuous drossing has several advantages over the batch process of dry stirring in kettles. Effective lead drossing by cooling is combined with the formation of matte and slag in a single process step. Handling of dusty copper dross is eliminated, which permits a major improvement in plant hygiene. Success in the development of a continuous drossing process has been achieved in Australia and the former Soviet Union by using a deep lead bath reverberatory furnace. The process is also employed at Cominco's lead smelter in Trail, Canada.

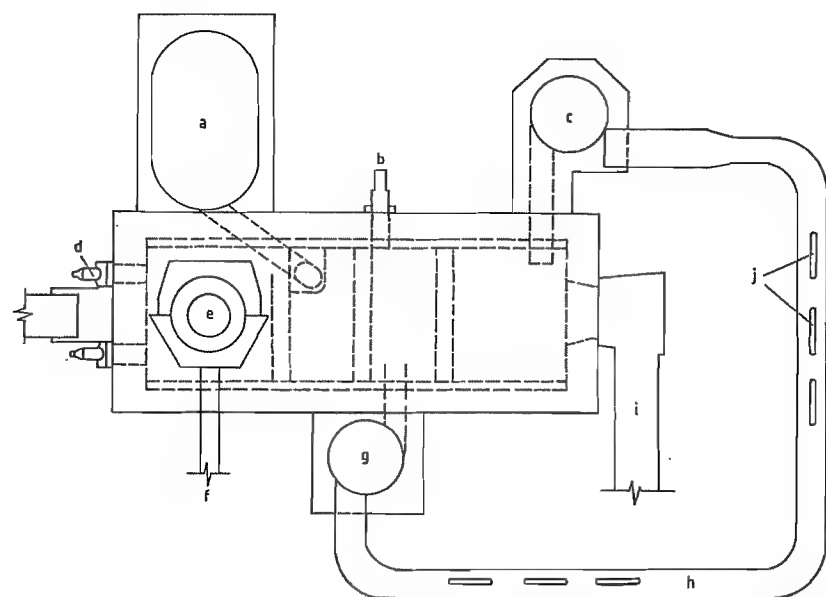


Figure 9.18: Plan view of the continuous dressing furnace of Broken Hill Associated Smelters (BHAS) at Port Pirie, Australia: a) Product dressed lead; b) Slag and matte tapping spout; c) Circulating pump pot; d) Gas burners; e) Charge port; f) Ventilation; g) Return launder pot; h) Cooling launder; i) Water-cooled flue; j) Water-cooled plates.

Figure 9.18 shows the furnace used by Broken Hill Associated Smelters (BHAS) in Port Pirie, Australia. The gas-fired furnace has an external bullion cooling launder (h) with immersible water-cooled plates (j). Hot bullion from the blast furnace is charged to the dressing furnace and is cooled by mixing with colder lead from the cooling launder. Dross formed rises to the heated surface and is melted to matte and slag. The third-generation furnace now used at Port Pirie has hearth dimensions of 6.15 m by 2.0 m and a depth of 1.7 m [24]. The process is best suited to refining lead with a fairly uniform impurity content. An important operating criterion is the ratio of copper to sulfur in the bullion. A high ratio causes the formation of high melting point speiss crusts in the furnace. Recent development has allowed addition of elemental sulfur to the furnace permitting satisfactory operation at bullion copper levels approaching three percent.

In the Russian continuous dressing process, bullion cooling is achieved by indirect water-cooling through the furnace bottom. Copper

drossing and cooling are finished in batch kettles, dross being recycled to the dressing furnace. Soda ash is added to the furnace to produce a low lead soda matte.

Sulfur Dressing. *Final decoppering* (sulfur dressing) is carried out *batchwise* in most plants in kettles fitted with a powerful stirrer. Fine sulfur is added in increments to the lead vortex at 330–340 °C, and the formed copper dross is skimmed, usually with the aid of sawdust. This dross is much lower in copper (and higher in sulfur) than primary decoppering dross and is returned to a convenient point in the smelting process. In industrial operation, about 1 kg of sulfur is added per kilogram of copper; the end copper content must be less than 50 g/t if possible. Several sulfur treatments are needed to achieve this.

A *continuous sulfur dressing system* has been developed by BHAS at Port Pirie [24] and has been operating since 1981. The process employs a series of small stirred kettles [23]. A continuous flow of bullion from the copper dressing furnace is cooled, treated with elemental sulfur, and mechanically drossed.

9.6.1.2 Removal of Arsenic, Tin, and Antimony

The removal of arsenic, tin, and antimony is called *softening*. Two processes are in use: selective oxidation with air in fired furnaces and the Harris process.

Oxidation in Air-Blown Furnaces. This method is based on the fact that tin, arsenic, and antimony react more readily with oxygen than lead, and are oxidized (in the order listed) before lead at 700–750 °C. Air is injected through vertical lances onto the surface of a lead bath in a rectangular oil- or gas-fired reverberatory furnace. The oxides of tin, arsenic, antimony, and lead form a fluid slag, which is periodically removed from the surface of the lead bath. A considerable amount of lead is oxidized and the slag generally contains 50–60% lead monoxide. In batch reverberatory softening, segregation of slag skimmings into high arsenic–tin and high antimony lots is possible, but not usually practised.

The oxides float on the molten lead and are withdrawn as softening slag. Refining time depends on the amount of impurities in the charged bullion and also on the air-lancing method. Impurity oxidation rates in the order of $4 \text{ kg m}^{-2} \text{ h}^{-1}$ are typical.

Continuous bullion softening is operated by BHAS, Port Pirie, Australia. Drossed lead is pumped continuously into a softening reverberatory furnace fitted with an air-lance system similar to a batch softening furnace. The rate of bullion feed and the rate of arsenic and antimony oxidation are such that the antimony content is maintained at 0.02–0.05%. Antimony oxidation rates of $40 \text{ kg m}^{-2} \text{ h}^{-1}$ are achieved, about an order of magnitude greater than in batch softening.

Harris Process. The Harris process employs molten sodium hydroxide as a medium for the oxidation of arsenic, tin, and antimony from lead bullion. Metallurgie Hoboken-Overpelt, Hoboken, Belgium [25] and the Norddeutsche Affinerie, Hamburg, Germany [26], use this process. Harris refining is performed

batchwise using a reaction cylinder holding molten sodium hydroxide installed in a lead kettle. Figure 9.19 shows one half of a dual kettle Harris reactor as employed at the Hoboken smelter. Bullion is pumped through the Harris reactor caustic charge until the required degree of impurity removal is achieved. A valve at the bottom of the caustic vessel is then closed allowing the loaded caustic to be discharged to a transport ladle for subsequent hydrometallurgical processing. Fresh molten caustic recovered from the salt processing plant is charged to the reactor by ladle for the next refining cycle.

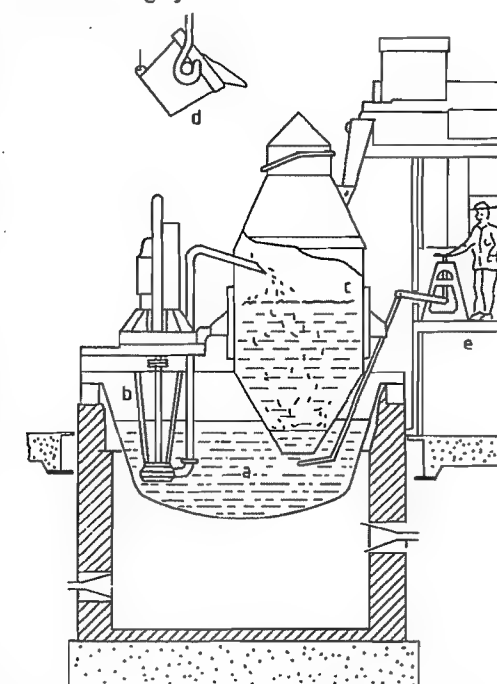
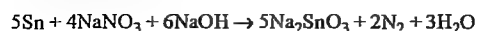
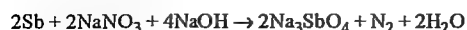
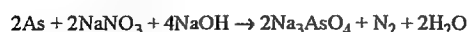


Figure 9.19: Harris reactor at Metallurgie Hoboken-Overpelt S.A. [25]. One half of the dual reactor is shown. a) Lead bullion; b) Lead bullion pump; c) Molten caustic holding vessel; d) Molten caustic supply ladle; e) Reactor control system.

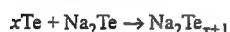
The Harris process is the preferred softening process for lead bullion containing high levels of impurities. The plant at Hoboken can remove up to 400 t of arsenic, tin, and antimony from lead bullion per month.

Harris softening involves the oxidation of arsenic, tin, and antimony by air or by sodium

nitrate added to the caustic bath. The oxidation products, in order of their formation, are sodium arsenate, sodium stannate, and sodium antimonate:



Tellurium is oxidized to sodium tellurate and telluride:



The arsenic salt is soluble in the molten caustic whereas the salts of tin and antimony form a solid suspension. Because of the reversibility of the oxidation chemistry (e.g., Na_3SbO_3 will oxidize arsenic and tin from bullion), a loaded caustic salt is produced that is high in arsenic and tin, followed by a salt containing primarily antimony. Table 9.4 gives the distribution of arsenic, tin, and antimony in the products of the Harris refining process at the Hoboken lead smelter. A flow sheet is given in Section 9.6.1.7 (Figure 9.24).

Table 9.4: Distribution of metals in products separated by the Harris process at Metallurgie Hoboken-Overpelt S.A. [23].

Product ^a	Metal, %		
	As	Sn	Sb
Lead particles As-Sn	5.5	5.0	2.1
Lead particles Sb	0.2	0.1	4.0
Black antimonate ^b	0.5	2.5	3.8
Calcium stannate	2.2	91.8	0.2
Calcium arsenate	91.6	0.5	0.3
White antimonate		0.1	89.6

^a For origin of products, see Figure 9.24.

^b Contains more than 80% of extracted Te, Se, and In.

9.6.1.3 Removal of Noble Metals

Noble metals and residual copper are removed from lead by the Parkes process in which zinc metal is added to the molten silver-bearing lead and the mixture is cooled (see also Chapter 24) Silver-zinc mixed crystals precipitate out and rise to the bath surface as a crust (Parkes process crust). The intermetallic compounds have a higher melting point than

lead and are virtually insoluble in zinc-saturated lead.

The metallurgical operations in the Parkes process are based on the lead corner of the ternary system Ag-Pb-Zn (Figure 9.20). Most of the silver removal takes place in the liquid + ϵ -phase Ag-Zn crystals region; the last crop of crystals in the latter part of the second stage comes from the liquid + η -phase region. Silver removal is very efficient and depends on the quantity of zinc and the number of stages used, but it is usually not economical to use more than two stages.

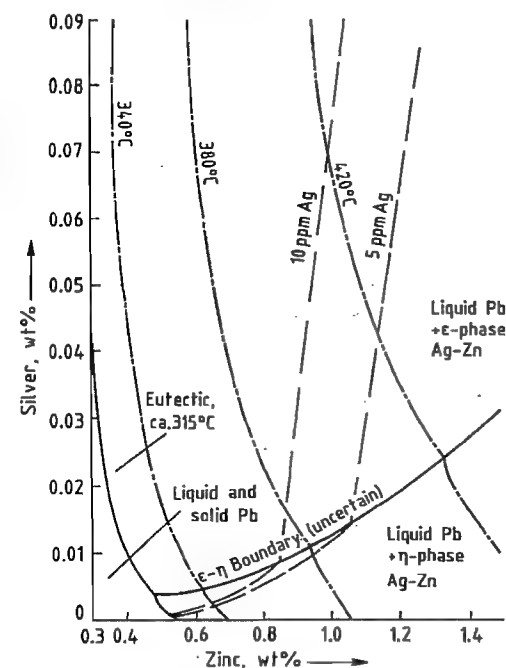


Figure 9.20: Lead corner of the Pb-Ag-Zn system in rectangular coordinates [23]. The isotherms (—) indicate how much zinc can be dissolved in the lead. The cooling curves (---) indicate the course of desilvering in the batchwise two-stage process for final silver concentrations of 5 and 10 ppm.

Process Engineering of Desilvering. In the *batch process*, desilvering is performed in two stages in kettles with capacities of up to 300 t. In the first stage "lean crust" from the preceding charge is added along with other recycle zinc and stirred into new softened lead at 460 °C. The "rich crust" is skimmed off for

silver recovery. In the second stage, zinc metal is added with stirring; more zinc silver crystals form, and the bath is then cooled to near freezing at about 370 °C so that the last crystals separate. At this point, the silver content of the near-freezing lead is 5–10 ppm.

The *Williams continuous desilvering process*, developed at Port Pirie, employs a deep kettle surrounded by heating jackets, which impose a vertical temperature gradient on the lead column from 600 °C at the top to the temperature of the ternary Ag-Pb-Zn eutectic at the bottom. The upper part of the column contains ports for the intake of lead, addition of zinc, and removal of the ternary alloy. A siphon for discharging the desilvered lead has its intake just above the bottom of the kettle.

The softened silver-bearing lead is brought to 650 °C in a conditioning furnace and then flows continuously into the desilvering kettle. The lead flows through the zinc layer in the upper part of the kettle, and becomes saturated with zinc. As it descends down the kettle, it is cooled along the imposed temperature gradient. When it approaches the freezing temperature, silver-zinc crystals precipitate and rise to the zinc layer at the lead surface. The desilvered lead contains about 3 ppm Ag and 0.6% Zn, and leaves the kettle through the siphon.

The composition of a fresh zinc layer changes, becoming enriched in silver (and lead). When it approaches about 15% silver, 20% lead, it begins to freeze. The mushy alloy is then ladled out and replaced with fresh zinc. Residual copper and any gold are removed very efficiently along with the silver. Continuous desilvering produces only a single silver-zinc crust which can be sent directly to distillation — an advantage over two-stage desilvering. The modern batch operation, however, uses less zinc and has lower operating costs.

9.6.1.4 Dezincing

The desilvered lead still contains about 0.55–0.6% zinc which must be removed. Older methods used air and steam, caustic soda, or chlorine, all of which oxidized the zinc metal. These have been replaced by vac-

uum distillation of zinc from the desilvered lead. The large difference in vapor pressure between the host lead and dissolved zinc permits the volatilization of about 95% of the zinc from the desilvered lead when a vacuum of about 0.133 Pa is applied at about 600 °C. A condensing surface placed close to the surface of the lead allows kinetic control of the distillation. The zinc content of the vapor exceeds the mole fraction in the melt by over 500% [23].

Process Engineering. *Batch dezincing* is performed in a kettle: a water-cooled bell is sealed vacuum-tight on the kettle and distillation is carried out at about 600 °C and a vacuum of about 0.133 Pa (measured at the pump). The lead is circulated by a stirring mechanism, also sealed vacuum-tight. Crystalline zinc precipitates on the bottom of the water-cooled vacuum bell and is struck off after the termination of the process. Adequate sealing was originally achieved by letting the bell dip into the lead bath (barometric seal); today, water-cooled gaskets are preferred.

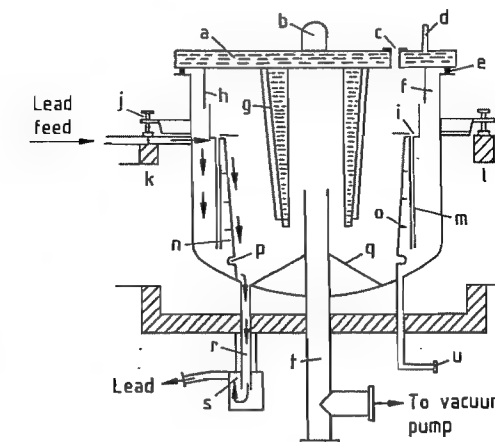


Figure 9.21: Continuous vacuum dezincing: a) Water-cooled cover; b) Hook; c) Window; d) Cooling water connections; e) Rubber gasket; f) Baffle; g) Cooling fins; h) Weir plate; i) Lead trough; j) Level control; k, l) Furnace setting gas entry and exit; m) Lead inlet to trough; n) Evaporation surface; o) Reinforcement; p) Flexible connection; q) False bottom; r) Lead outflow; s) Lead siphon; t) Vacuum connection; u) Drain.

At Port Pirie, continuous dezincing has also been developed. The dezincing apparatus

(Figure 9.21) consists of a thin-film evaporator with roughly 0.75 m^2 of evaporating surface. It can dezinc 16–37 t/h of Parkes lead, and 90–95% of the zinc content is recovered on a water-cooled fin condenser. When about 3 t of zinc has been collected, the condenser is replaced. The deposited zinc is melted and returned to the desilvering operation.

The lead is heated to 590–620 °C in a pre-heat furnace, before entering the vacuum kettle. After dezincing, it leaves the unit at 540–560 °C with a zinc content of about 0.03%. The pressure inside the kettle is 3–7 Pa. The residual zinc in the lead bullion is removed during final refining.

9.6.1.5 Debismuthizing

Debismuthizing is the last step of lead-bullion refining. It is applied when the bismuth content of the ore is so high that it restricts the use of the soft lead smelted from it. When possible, bismuth-rich and bismuth-poor ores are smelted separately in order to refine the minimum amount of lead bullion with the maximum bismuth content.

Bismuth is less reactive than lead, therefore it cannot be removed with oxygen, chlorine, or sulfur. It is customarily separated by addition of an alkali metal or alkaline earth metal forming a bismuthide M_xBi , but this only permits a minimum bismuth content of 0.03%, which is not adequate for many requirements. The removal of bismuth to < 0.01% can be achieved by the *Kroll-Betterton process*, which uses calcium and magnesium and also by the *Jollivet-Penarroya process*, which uses potassium and magnesium. Only the former remains in use; the metallurgical reactions take place in the lead corner of the corresponding quaternary system (Figure 9.22). Bismuth separates as a crust of the double bismuthide, CaMg_2Bi_2 .

The lowest attainable bismuth content is around 0.002% at the quaternary eutectic point. Further addition of calcium and magnesium does not improve bismuth removal. The reagent requirement is given by the total calcium and magnesium needed for precipitation

as the double bismuthide and for saturation of the lead.

Process Engineering. The Kroll-Betterton batch debismuthizing process is carried out in kettles. Magnesium and calcium (in lead) are stirred into the lead bath at a temperature of about 420 °C. The bath is then cooled to near the solidification point with slow stirring. The crust (enriched about 10:1 in bismuth) is removed in a similar manner to the Parkes process. The crust grade can be improved considerably by stirring into the next batch of lead. Both batch and continuous versions of the Kroll-Betterton refining are practiced. A procedure is also used for secondary, fine debismuthizing by antimony addition [27].

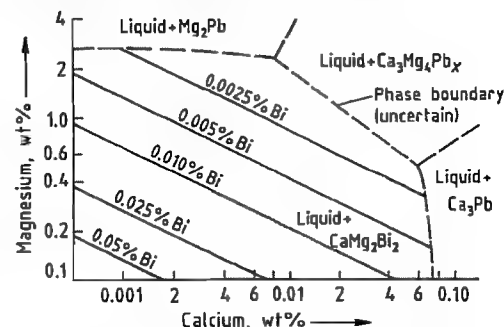


Figure 9.22: Lead corner liquidus of the quaternary Pb-Bi-Ca-Mg system [23].

9.6.1.6 Final Refining and Casting of Lead

Refined lead contains arsenic, antimony, and tin at a level of 10–20 g/t; zinc corresponding to the final content in vacuum dezincing (ca. 30 g/t); and (if debismuthizing has been performed) calcium and magnesium corresponding to the saturation limit. These impurities are removed down to below 1 g/t by treatment with caustic soda and, in some instances, with sodium nitrate.

Most casting today is done automatically in strip or (less often) bench form, in machines provided with automatic stacking devices. The casting temperature is around 400 °C. Immediately after admission to the chill mold, the thin oxide surface film is skimmed off. The

cast lead has a coarsely crystalline surface; if final refining and casting techniques are correct, there are no temper colors.

9.6.1.7 Processing of Intermediate Products of Pyrometallurgical Refining

Copper Dross. Copper dross is a complex mixture of compounds and contains a substantial amount of sulfidic and metallic lead. Melting the dross in a retreatment furnace frees the metallic lead and forms a matte phase, consisting mainly of lead and copper sulfides, and a slag which contains metal oxides and often requires silicate fluxing. If arsenic is available and sulfur is deficient, a copper arsenide speiss product is formed. The slag is returned to the smelter, but the matte is a product for sale or further processing.

All constituents of the dross deport to the four possible liquated phases lead, speiss, matte, and slag. If large amounts of arsenic are present, a speiss forms in which nickel, arsenic, and part of the copper are preferentially concentrated. If copper and arsenic levels in the dross are low, the matte and speiss must be enriched by a further treatment. In dross retreatment, it is desirable to minimize the lead content of the final matte. If the iron and sulfur contents are known, the final lead content can be approximately estimated from Figure 9.23: % Fe is equated to % (Fe + Zn) in the lead-free matte and % S can be determined from the lead-free sum, $\text{Fe} + \text{Zn} + \text{Cu} + \text{S} = 100\%$. For example, for a lead-free matte containing 7% Fe, 1% Zn, 24% S, and 68% Cu, the lead content predicted from Figure 23 is 20%. The final matte would then contain 20% Pb, 5.6% Fe, 0.8% Zn, 19.2% S, and 54.4% Cu. This is a fair estimate only for low alkali mattes. Sodium or calcium additions lower lead solubility in the matte substantially; at 5% sodium or calcium the solubility is reduced to less than 20% of that in the same matte without alkali. This is the basis of the soda matte process used by Asarco (El Paso) and St. Joe Lead at Hercules, in which about 5% soda ash is added

to the dross during melting and produces a copper enriched matte.

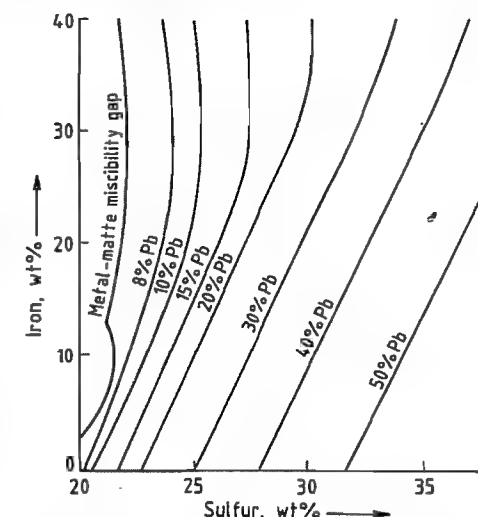


Figure 9.23: Solubility of lead in Cu-Fe-S mattes [23].

The recovered lead contains most of the noble metals. Matte, and particularly speiss if present, also hold significant amounts of precious metals. Fume from the furnace is enriched in indium, tin, arsenic, and zinc. Slag, matte and speiss are normally granulated.

Hydrometallurgical methods for treating copper dross involve solubilizing the copper for electrowinning either by pressure oxidation leaching in sulfuric acid or by ammoniacal leaching and solvent extraction.

Softening Slags and Drosses. Softening slag and skimmings with variable contents of tin, arsenic, and antimony are usually reduced to hard lead. An effort is made to slag off part of the arsenic during reduction. The process is normally carried out in a rotary furnace, but can also be done in a blast furnace.

In the short rotary furnace at Port Pirie, 7 t of softening slag are reduced batchwise with the addition of 5% soda, 7% charcoal, and 6% "caustic slag" from subsequent refining. The charcoal is added in two portions. After the first portion is reacted, a lead bullion containing 2–3% antimony is tapped off and recycled. After the second reduction, about 85% of the

feed antimony is tapped off as an alloy containing 25–30% antimony.

Harris Salt Slags. Harris slags are processed to recover a large portion of the valuable minor metals as black antimonate (Sn, Sb, Te, Se, In) and sodium antimonate (Sb); to precipitate the tin as calcium stannate and arsenic as calcium arsenate; and to recover caustic soda for reuse. The flowsheet of Metallurgie Hoboken–Overpelt is shown in Figure 9.24.

Silver–Zinc Rich Crusts for Desilvering. The purpose of processing the silver–zinc-rich crusts is to recover a malleable rich lead that contains all the noble metals. Some of the lead and as much as possible of the zinc must be removed; the latter is reused. Removal is achieved by expression and/or liquation with

production of a dry or liquated crust, followed by zinc distillation.

Expression is commonly carried out in an air-driven Howard press submerged in a liquid lead bath, and the lead content of the compressed crust is brought to 50–60%.

Liquation. Alternatively the crust may be melted at about 600 °C under a salt cover and separated into a lead-rich lower layer, which is returned to desilvering, and a zinc-rich upper layer which passes to zinc removal.

Distillation allows the zinc content of the liquated rich crusts to be recovered in metallic form so that it can be reused for desilvering lead bullion. Distillation can be performed either at STP in the Faber du Faur furnace or under vacuum in the Leferrer furnace.

In the older *Faber du Faur* furnace, liquated zinc-rich crust is placed in inclined bottle-shaped graphite retorts and heated to 1000–1500 °C. Zinc condenses in a separate receiver in liquid form and is tapped off periodically. A certain amount of dross (zinc dust) is also formed; since this contains noble metals, it is recycled to the process.

A more modern method is the *Penarroya–Leferrer vacuum distillation* with radiation heating. This runs at a temperature (600 °C) well below the melting point of silver and considerable lead must be added to the crust to hold the silver in solution when most of the zinc has gone. The zinc condenses as a liquid. Low frequency induction furnaces are also used.

The distillation residue consists of silver containing other precious metals, zinc, lead, and copper. Zinc, lead, and copper are removed by cupellation (air oxidation), and the silver bullion is separated from gold by electrolysis. The cathode silver can be further refined by chlorination.

Bismuth Drosses. Bismuth dross can be processed by either pyrometallurgical or electrolytic methods. In either case, the reagents calcium and magnesium are first removed, so that the subsequent operations are always performed on a pure lead–bismuth alloy.

Lead is removed by selective chlorination of the lead–bismuth alloy with chlorine gas, lead being converted to lead chloride with virtually no loss of bismuth. The rate of lead chlorination in lead bismuth alloys with > 85% bismuth is extremely high at 700–800 °C. In practice, chlorine is injected into an alloy already enriched to this level, and lean material is simultaneously added. Operation is thus continuous and material throughput is constant. The crude bismuth usually has a low foreign element content (copper, noble metals), which is removed by a process similar to that used for the refining of lead bullion.

In comparison with the pyrometallurgical technique, the electrolytic method has the advantage that the lead is deposited in pure form at the cathode (generally as fine lead). The an-

ode slime from electrolytic lead–bismuth separation is subjected to reduction melting; the product is an alloy containing > 90% bismuth along with lead, copper, and noble metals. This alloy can be processed pyrometallurgically (selective chlorination) or by bismuth electrolysis.

9.6.2 Electrolytic Refining of Lead Bullion

The electrolytic refining of lead bullion from soluble anodes has been practised for years in a number of large plants. Because the poor solubility of lead sulfate rules out sulfate electrolysis, the only candidate electrolytes are the few readily soluble lead salts. In practice, solutions used have been restricted to the lead salts of fluosilicic acid (H_2SiF_6), fluoboric acid (HBF_4), and amidosulfuric (sulfamic) acid ($\text{H}_2\text{NSO}_3\text{H}$). The most important of these is the fluosilicate electrolyte.

Metals with a higher electrochemical potential than lead (silver, gold, copper, bismuth, antimony, arsenic, and germanium) remain essentially undissolved and accumulate in the anode slime, which is processed to recover them. Metals with a lower potential, such as iron, nickel, and zinc do go into solution, but the feed lead bullion contains such low levels of them that enrichment in the electrolyte is insignificant. The deposition potential of tin, -0.140 V, is close to that of lead, -0.126 V. Tin is therefore deposited along with lead from both fluosilicate and fluoborate electrolytes. The amidosulfate electrolyte, on the other hand, allows separation of lead and tin because of the low solubility of tin sulfamate.

The undissolved impurities, if they are present in large enough quantities, form a porous skeletal coating (slime). The slime adheres to the anode and retains its initial form, so that cells need not be regularly cleaned and deslimed. The mechanical strength of the slime depends on the content of foreign metals in the anode. Higher contents of bismuth and antimony enhance strength; increasing copper leads to a dense slime, so that the feed must be decoppered to < 400 g/t copper. The produc-

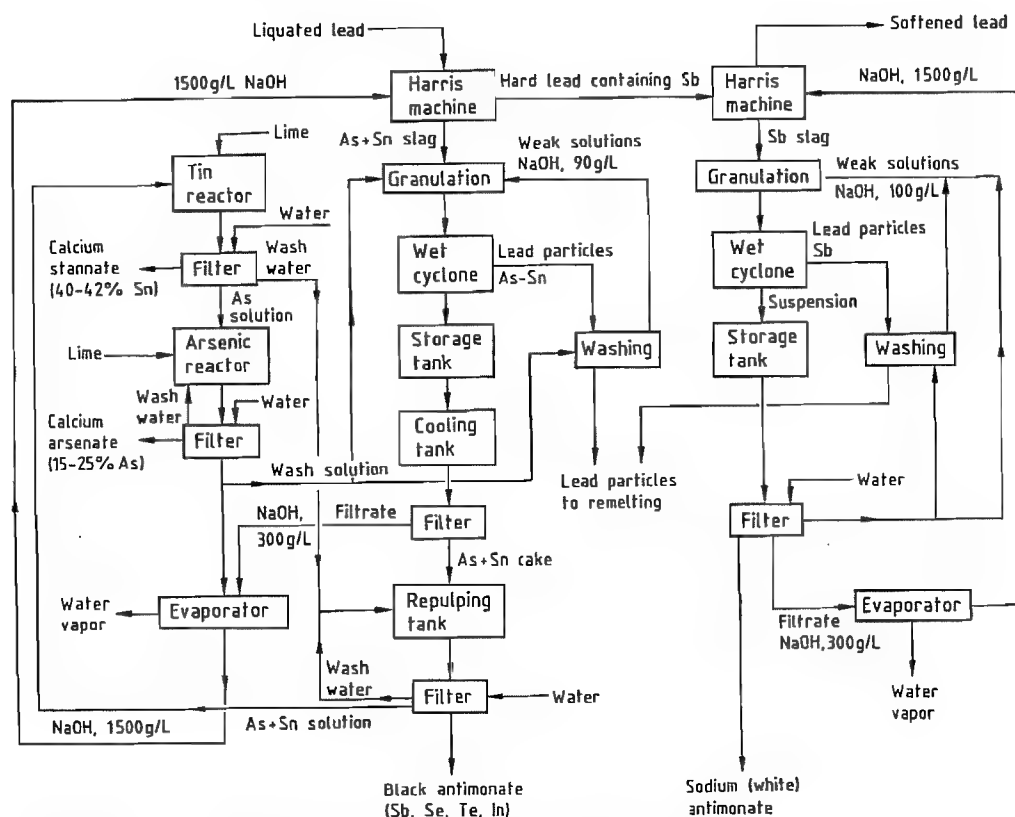
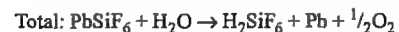
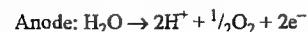


Figure 9.24: Treatment of Harris salt slags at Metallurgie Hoboken–Overpelt S.A. [25].

tion of adherent anode slimes requires a minimum antimony and bismuth content of 1–1.2%. The cell voltage rises with increasing thickness of the slime coating and may reach up to twice the initial voltage; thus, energy consumption imposes an economic limitation. In addition, the increasing voltage can lead to dissolution of antimony, arsenic, and bismuth from the slime. The residence time of the anodes in the cell, is governed by this rise in cell voltage and thus by the concentration of impurities in the anode lead.

In industrial electrolytic lead refining, the *Betts process*, an aqueous solution of fluosilicic acid and lead fluosilicate (PbSiF_6) is electrolyzed. One liter of electrolyte contains 60–100 g lead as fluosilicate and 70–120 g free H_2SiF_6 . Glue and/or other organic inhibitors (300–500 g per tonne of electrolytic lead) are added to obtain smooth deposits. Electrolyte losses result from the decomposition of H_2SiF_6 and entrainment in the anode slime.

The consumption of H_2SiF_6 is around 2 kg per tonne of electrolytic lead. The lead content of the electrolyte rises slowly because of the difference in current efficiency between anode and cathode. This increase is sometimes offset by precipitation of lead sulfate after addition of sulfuric acid. However, the lead content is usually held at the desired level by electrolysis in separate cells with insoluble graphite anodes. The following reactions take place:



Cathode blanks are made of electrolytic lead and are 0.8–1 mm thick. They are fabricated either by casting over an inclined plane (older procedure) or with a water-cooled drum that dips into the lead bath. One or two cath-

ode changes are generally required per anode. Current densities are 150–240 A/m^2 at the anode and 130–220 A/m^2 at the cathode. Current efficiency is 85–95% and energy consumption about 190 kWh per tonne of electrolyte lead. After electrolysis has been completed the anodes have about 30–40% of their starting weight and are melted down into new anodes. The cathodes are thoroughly cleaned, melted down, refined with soda in a kettle to eliminate residual antimony, arsenic, and tin, and cast into ingots.

The size and weight of the electrodes used for lead electrolysis at the Cominco lead refinery in Trail, Canada are given in Table 9.5. Other important data follow [28]:

Lead electrorefining data, Cominco Trail plant

Electrorefining cells	
Number	800
Dimensions (length × width × height), mm	2750 × 800 × 1250
Capacity, m^3	2.7
Material	polymer-containing concrete

Typical operating data
(based on lead production of t/a 120 000)

Anodes per cell	24
Cathodes per cell	25
Anode to anode spacing, mm	110
Current density, A/m^2	
Cathodes	130–220
Anodes	150–240
Current efficiency, %	80–90
Refining cycle, d	5
Cell voltage, V	0.3–0.5
Power consumption for electrolysis, kWh/t	168
Power consumption for other purposes, kWh/t	50
Hydrofluosilicic acid consumption, kg/t	2
Aloes extract consumption, kg/t	0.17
Lignin sulfonate consumption, kg/t	
Electrolyte temperature, °C	35–42
Electrolyte circulation to cell, L/min	20–25

Analyses

Anode, %	1.0–1.2 Sb, 0.3–0.6 As, 0.04–0.07 Cu, 0.1–0.2 Bi, 0.1–0.6 Ag
Cathode, g/t	3Cu, 8Bi
Anode slime, %	40–50 Sb, 20–30 As, 10–20 Pb, 5–15 Bi, 5–15 Ag
Electrolyte, g/L	60–70 Pb, 80–100 H_2SiF_6

Table 9.5: Size and weight of anodes and cathodes used at the Cominco lead refinery.

Immersion dimensions	Starter cathode	Plated cathode	Starter anode	Corroded anode
Length, mm	900	910	860	850
Width, mm	660	680	660	650
Thickness, mm	1	20	30	10
Area, m^2	1.2	1.25	1.2	1.15
Approximate weight, kg	6	140	200	60

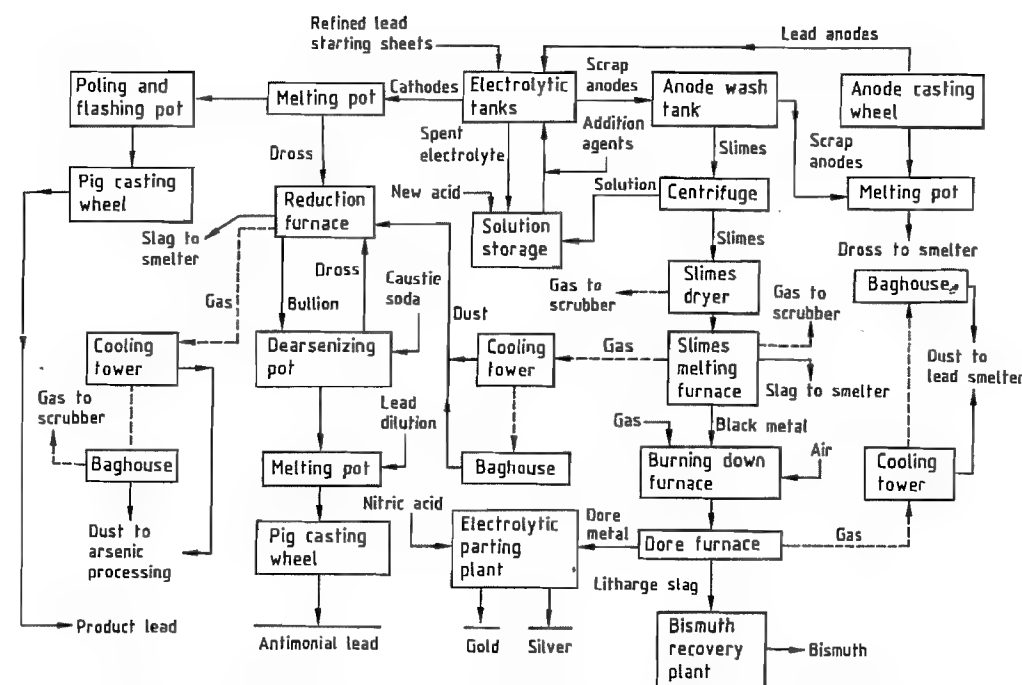


Figure 9.25: Flowsheet for electrolytic lead refining and slime treatment of Cominco Ltd. (Trail, Canada).

Processing of Anode Slime. The composition of the anode slime depends directly on the impurities in the anode lead. In general, anode slime contains not only noble metals but also high levels of bismuth and antimony. Different compositions are seen at plants that have modified their operation for bismuth recovery. For example, at the Norddeutsche Affinerie, the anode lead consists of bismuth drosses and high-bismuth lead that has gone through the entire thermal refining process except for Kroll–Betterton debismuthizing.

No single processing method has been devised for such diverse intermediate products. By way of example, Figure 9.25 presents the flowsheet of the Cominco refinery in Trail. The combination of proven pyrometallurgical processes yields product lead, doré (gold–silver), antimonial (hard) lead, and bismuth metal. The complexity of anode-slime processing places some restrictions on the inherently elegant electrolytic refining technique.

9.7 Recovery of Secondary Lead from Scrap Materials

The total world production of refined lead in 1987 was estimated to be 5.6×10^6 t. Of this approximately 60% was primary lead from lead ores and concentrates; the remainder (40%) was secondary lead produced from scrap materials. As the consumption of lead for sheet, pipe, and cable sheathing has declined and consumption for lead acid storage batteries has increased, the secondary lead industry is primarily concerned with the processing of scrap batteries. In recent years the industry in the United States, and to a lesser extent in Europe, has experienced new, more stringent environmental regulations, and very low lead prices in the mid-1980s. These factors have brought about the closure of a large number of small-scale secondary processing operations, and provided the impetus for the development of improved technology. Besides improving plant working conditions and re-

ducing ambient lead emissions, an important objective of new environmental regulations is to force the efficient recycling of lead-acid batteries and prevent disposal in municipal waste sites. The potential generation of acetic acid and contamination of ground water with soluble lead acetate is the basis for this regulatory pressure. In Germany the efficiency of spent battery recycling is claimed to be 90%.

9.7.1 Battery Types and Composition

Lead-acid storage batteries are of three general types:

- SLI (Starting, Lighting, Ignition) batteries, the bulk of which are automotive;
- Traction vehicle batteries; and
- Stationary batteries for supplying emergency power.

The key components in all these types are:

- a polypropylene containment box
- grids, connectors, and poles of lead alloy
- electrode paste: mixture of lead sulfate and lead oxides
- grid separators of poly(vinyl chloride) (PVC)
- sulfuric acid

The approximate composition of these materials on a weight percentage basis is:

Lead alloy components	21
Lead oxide	16
Lead sulfate	24.5
Water and sulfuric acid	24
Polypropylene	7.7
Poly(vinyl chloride)	3.8
Others	3.0

9.7.2 Battery Breaking and Processing Feed Preparation

Scrap battery preparation has progressed through four levels:

1. Acid drainage followed by pyrometallurgical processing of the entire battery and case. This blast furnace smelting approach became increasingly difficult with

the change from bakelite to easily-fused polypropylene battery cases [27].

2. Separation of acid and case, both of which went to waste as gypsum (after neutralization with lime) and plastic garbage, respectively. The remaining mixture of poles, grids, grid paste, and PVC separators became secondary smelter feed.
3. Mechanical shredding of batteries followed by heavy medium separation to produce
 - Drainage acid for sale or limerock neutralization to produce gypsum as waste
 - Clean polypropylene for sale and recycle
 - A clean metallic fraction which can be smelted at low temperature
 - Battery paste mixture of PbSO_4 and PbO_x
 - Clean PVC plastic to waste or recycle
4. The same as (3) except that battery paste and drainage acid are reacted with sodium carbonate to produce dry crystals of sodium sulfate, a saleable product [28]. This system has several advantages. The sulfur content of the lead-bearing feed materials is largely eliminated, thus simplifying the subsequent smelting processes and reducing the amount of waste sulfur and lead-bearing slag. Figure 9.26 shows the flow-sheet of the Tonolli CX process as an example.

9.7.3 Smelting of Battery Scrap Materials

The metallurgical equipment used for treating battery scrap consists of blast furnaces, reverberatory furnaces, rotary kilns, and short rotary furnaces.

Blast Furnace Treatment of Battery Scrap [29–32]. Typical blast furnace charge consists of cased batteries and battery plates with paste, limestone flux, scrap iron, metallurgical coke, and miscellaneous recycle drosses and slags.

Blast furnaces used for battery scrap smelting are smaller than primary lead industry blast furnaces. Typical hearth areas are in the range of 2–5 m². Smelting products are lead

bullion containing most of the antimony content of the charge, iron matte containing most of the sulfur in the charge, slag, and flue dust which must be melted or agglomerated for recycle.

Plastic materials in the charge can, through fusion, impede the flow of material in the furnace shaft. This adverse effect is controlled by recirculating crushed slag in the furnace charge. Volatile organics in the off-gas must be combusted in an afterburner to prevent bag-house operating problems.

With advanced battery feed preparation systems, the role of the blast furnace in the industry is expected to decline in favor of reverberatory or rotary furnace reduction of lead carbonate-oxide sludge and metallic grid products.

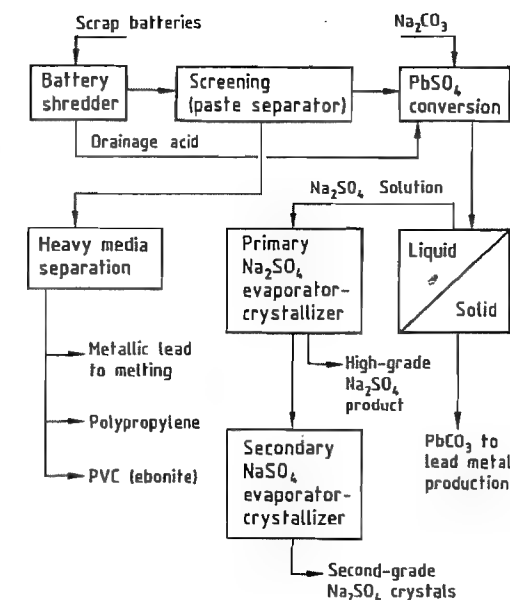


Figure 9.26: CX scrap battery components recovery plant.

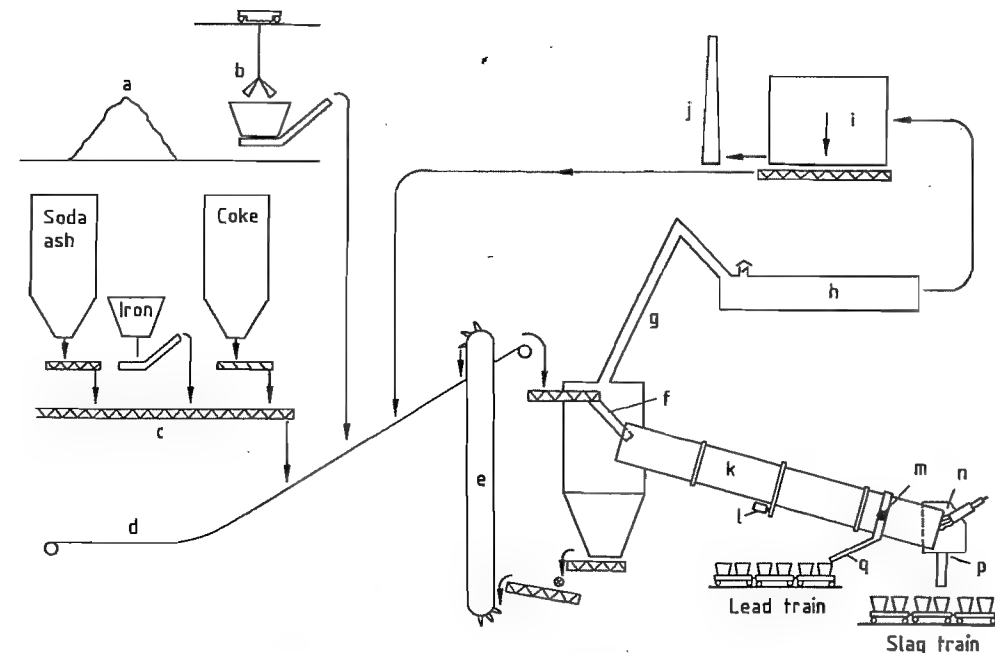


Figure 9.27: Rotary kiln scrap battery smelting plant: a) Buffer storage building; b) Bucket crane; c) Flux feed conveyor; d) Main feed conveyor; e) Bucket elevator; f) Feed chute; g) Vee duct; h) Balloon screw; i) Baghouse; j) Stack; k) Kiln; l) Kiln drive; m) Tap hole; n) Burner head; o) Burner; p) Slag chute; q) Lead train; r) Slag train.

Rotary Kiln Smelting of Secondary Lead.

Continuous processing with long rotary kilns was developed by Preussag AG, Goslar, Germany, and is practised in several other locations [33]. A typical equipment layout for this type of plant is shown in Figure 9.27. The kiln charge consists of a plastic-free mixture of sulfate, lead posts, grids, metallic iron, soda ash, coke breeze, and recycle flue dust. Products are lead bullion and a mixed matte slag material for discard.

Short Rotary Furnace Smelting. The short rotary furnace is extensively used for smelting battery scrap materials [34]. Typical furnace dimensions are a diameter of 3.5–4.0 m and a length of 4–5 m. Reverse-flow firing is usually employed with the combustion burner and gas offtake at one end of the furnace. The charge components and general metallurgy are very similar to the rotary kiln process. The main difference is batch rather than continuous operation, which allows the use of different charges for the production of high- or low-antimony bullion products.

Reverberatory Furnace Smelting. The reverberatory furnace, although generally less productive than rotary furnaces, provides good control of the reduction potential required to produce low-antimony bullion and retain antimony in slag for subsequent reduction to high-antimony bullion. Reduction of desulfurized battery paste is also readily achieved at low temperature in reverberatory furnaces.

9.7.4 Future Trends

Increased environmental pressure is expected to continue to force innovation in secondary lead recovery. Slags produced by thermal reduction processes are classified as hazardous waste in the United States. Further electric furnace reduction of slag is now being practiced by the RSR Corporation in the United States to make slags acceptable for non hazardous disposal.

The lead–acid (SLI) battery industry is changing to sealed low-maintenance designs which require high-purity lead for the calcium lead alloy grids. The secondary industry has been forced to produce an increasing percentage of high-purity lead compared to the grades of antimonial lead produced in the past. Removal of antimony by kettle caustic softening is costly. The incentive to separate battery scrap into low-antimony paste and high-antimony metallic components for separate processing is thus expected to increase.

The search for nonthermal processes for high-purity lead recovery, particularly from desulfurized battery paste, is expected to intensify. Research work by the U.S. Bureau of Mines [35], and the RSR Corporation in the United States and Technologic Tonolli (Italy) on a fluosilicic acid leach electrowin method of treating lead carbonate oxide paste is expected to be used commercially in the early 1990s.

9.8 Uses

The trend in end-use consumption of lead over the period 1977–1987 is illustrated in Table 9.6 for the United States, Japan, and Western Europe. A more thorough breakdown compiled by the Lead Development Association and the Lead Zinc Study Group for presentation to the “Metals 2000” Conference is drawn upon for the following analysis.

Lead batteries were responsible for 60% of refined lead consumption in the Western world in 1987 (ca. 2.5×10^6 t). The battery market is by far the largest end use of lead. It has shown a steady growth rate of 6% from 1984 to 1989, corresponding to the increase in the number of automobiles worldwide. Automotive batteries for starting, lighting and ignition (SLI), traction batteries, and stationary batteries account for 75, 10, and 15% of total battery lead consumption, respectively.

Table 9.6: Consumption of lead by end-use (%) (Source: Metallstatistik 1977–1987).

Use	United States		Japan		Europe ^a	
	1977	1987	1977	1987	1977	1987
Batteries	59.8	77.5	49.6	68.7	38.4	44.6
Cables	0.9	1.6	10.1	1.7	11.0	7.0
Semifinished	7.0	6.7	8.2	3.0	16.8	17.5
Pigments and chemicals ^b	21.0	7.6	15.0	16.2	25.4	22.3
Alloys	7.2	4.4	5.1	4.6	4.4	3.4
Other	4.1	2.2	12.0	5.8	4.0	5.2
Total	100.0	100.0	100.0	100.0	100.0	100.0
Total, 10^6 t	1.436	1.230	0.334	0.378	1.164	1.131

^a Germany, France, United Kingdom, Italy.

^b Includes antiknock compounds.

SLI batteries represent the predominant use of lead. In 1987 about 160×10^6 batteries were used in new cars and for replacements in a world car population of over 500×10^6 . The number of vehicles is expected to increase, and so should lead use in batteries. The content of lead and lead compounds in battery walls, grids, and coatings has been steadily reduced to improve performance, minimize weight, and extend lifetimes. This has contributed to much better operating economics. The vehicle battery market is obviously vulnerable to substitution by other elemental couples and chemistry, but so far no competition appears likely to have a serious impact. Other factors that could affect future SLI battery use are increasing power requirements of cars and haulage vehicles, which would demand more powerful batteries and the possible use of higher voltages.

Traction batteries are used to power electric vehicles which have low running costs and are quiet and pollution-free. The vehicles are commonly used in short-range commercial delivery applications, in airports, and as fork lifts. The heavy weight and limited capacity of the conventional lead acid battery seriously restrict vehicle speed and operating range between charges. It is unlikely that the lead battery will power a successful design of passenger vehicle.

Stationary batteries are used for standby and emergency power supply. Besides emergency lighting, special applications involve computer installations, process control sys-

tems, and emergency power in aircraft and trains. The market is growing. A new market is developing for small, sealed cells used in safety and security systems and personal computers.

Pigments and Lead Compounds. After batteries, the next largest use of about 14% of refined lead is in glass making, ceramic glazes, plastic stabilizers, and paints. Lead glass has desirable optical, electrical, and radiation shielding properties, and lead crystal glass in particular is in great demand. Although ceramic glazes for tiles, tableware, and fine china have declined in application because of concern about lead's toxicity, they remain a significant part of the compound market. Lead compounds used for stabilizing PVC against temperature and UV light are finding intensive competition from other, more environmentally acceptable stabilizers. The lead pigment market is now very small.

Semifinished Products. Rolled and extruded lead, mainly sheet and pipe, account for about 8% of total lead use. Piping was formerly the greater part of this sector, but toxicity concerns and substitution by plastics and copper have reduced the market considerably. The use of lead sheet for roofing, restoration of old buildings, sound insulation, radiation shielding, and chemically resistant linings is now greater than that for piping and is growing steadily.

Cable Sheathing. A major area of lead use was in the protection of electrical and tele-

communications cables, but this market has declined drastically since the early 1960s due to substitution by aluminum and plastics. Nevertheless, this application still accounts for about 5% of total lead use, and there now appears to be a return to thin lead sheathing as a total moisture barrier in association with plastic sheathing.

Lead Alloys. Solders, type metal, bearing alloys containing lead still account for about 4% of the lead consumption. Type metal usage has nearly disappeared, but the bearing metal market is still reasonable in spite of some substitution. Uses of lead-base solder are growing, as electronic products find increasing markets which outweigh the trend to miniaturization and inroads made by tin.

Gasoline Additives. In 1972 the use of tetraethyl lead for improving the octane rating of gasoline was nearly 400 000 t/a. Since then, this sector has declined dramatically by 70%, principally in the United States. The reason has been the proscription of lead antiknock compounds by environmental legislation. The tetraethyl lead market, now 3% of lead use, can be expected to disappear with the eventual departure of older vehicle engines that require leaded gasoline.

Shot and Ammunition. Shot and ammunition account for about 2% of lead consumption and represent a steady market. Lead shot is used in alloying steel and brass to free machining metals, and for shotgun cartridges.

Miscellaneous. Uses that do not fall into the above categories account for about 4% of lead use, and include products featuring the high density of lead such as wheel weights, yacht keels, ornamental items, stained glass, and massive radiation shielding.

Much work is being done by lead concerns to identify and develop new applications for the metal. Promising new uses include lead levelling battery banks used by utilities or by major power consumers to reduce high-cost peak power consumption; lead containers for disposal of radioactive waste; and asphalt sta-

bilizers for retarding road paving deterioration.

9.9 Economic Aspects

9.9.1 Lead Concentrate Schedules

Most lead smelters operate with a concentrate supply from associated mines. A few "custom" smelters (e.g., at Hoboken) purchase essentially all reed materials on the open market. In rare cases a smelter will agree to "toll" a concentrate, whereby the concentrate supplier pays for the processing of his material as part of the smelter's overall charge, and receives the recovered metal for his own use.

Lead concentrate from the beneficiation of lead-zinc or lead-zinc-copper ores is the primary feed for blast furnace and flash smelters. Smelters employing the Imperial Smelting process generally use mixed lead-zinc concentrates. Conventional lead concentrates consist of galena in a sulfide matrix; the lead content is usually well over 60%. The concentrate may also contain zinc and iron sulfides; gangues such as silicon dioxide, calcium oxide, magnesium oxide, and aluminum oxide; and a number of minor metal impurities that may be partially or totally recovered and which may also cause smelting or refining problems. The price assigned to a concentrate by a smelter reflects its own priorities and the suitability of the concentrate for the operation, as regards its valuable components and impurities. Smelters reject concentrates with elements that adversely affect metallurgy or refining practice. Examples are rejection of a high-sulfur (low-lead) concentrate by a down-draft sintering operation or of a bismuthic concentrate by a refinery without a capability for bismuth removal and recovery.

In compounding the aggregate feed and in selecting concentrates for purchase, lead smelter metallurgists and ore buyers balance the inputs of all valuable and harmful elements to create a charge that can be handled effectively and consistently within the limits of the operating processes, and with maximum

profit. The pattern is set by the major concentrate supplies, usually from in-company sources: other raw materials are obtained to fit objectives of output, quality, cost, and timing.

A lead smelter's purchase schedule for lead concentrates comprises identifications and rules that govern payments for certain components, penalties levied on the presence of others, occasional bonus payments or penalties for desirable or undesirable combinations, and a treatment charge designed to cover smelting and refining costs and allow for profit. Most smelters can make available a general or "open" schedule set out in sufficient detail to cover a wide range of raw materials, but this is applied only to small lots. Major long-term purchases are normally made on the basis of a negotiated schedule. The schedule of purchase terms also covers sampling, assay of constituents and moisture, settlement of disputes, reference metal prices for determination of paid values, currency exchange, escalation of costs and prices, and payment terms.

Through its applied schedules, a lead smelter always pays for lead, silver, and gold, often for copper and zinc, sometimes for bismuth, and very rarely for antimony, platinum, palladium, or indium. Lead payment is offered on about 95–97% of the contained lead at a defined lead price. A blast furnace or flash smelter prefers lead content > 60%, but an ISP smelter accepts lower lead content, particularly with associated substantial copper value. Silver and gold are routinely recovered at high efficiency by lead refineries, and are paid for at current prices subject to minimum deduction from the assayed content, reflecting the minor losses, and to a treatment charge.

A payment may be offered for contained zinc if the smelter processes high-zinc charges by slag forming but additional costs for fluxes and fuel are assessed against the payment. The ISP smelters routinely pay for zinc subject to minimum deduction and a treatment charge. Iron is a major component of lead smelting slag and is of particular value in fluxing zinc, but may be present in excess of requirement and would then incur a modest penalty.

Most blast furnace and ISP smelters pay for copper, which is usually recovered in drossing as matte, subject to minimum deduction and treatment charge. ISP smelters can handle higher copper inputs than other lead smelters.

Arsenic is always heavily penalized under lead smelter schedule terms from levels as low as 0.05%; this reflects the uncompensated problems arsenic creates in refining, hygiene, and environmentally acceptable disposal. Antimony is usually neither paid for nor penalized.

Bismuth's treatment in a lead smelter schedule depends on whether the refinery can separate and recover the metal comprehensively (as in electrolytic refining) or by pyrometallurgical debismuthizing at high unit cost. More often it would be a reason for rejection of the concentrate. Certain smelters can recover tin, indium, cadmium and thallium in the sintering, drossing, and refining circuits but these elements are never paid for. Thallium may be the cause of rejection by an electrolytic refinery and tin by an ISP zinc-lead smelter.

Lime and silica are desirable fluxes in lead smelting and are usually assigned minor credits in a lead schedule. Blast furnace smelters may penalize alumina for its deleterious effect on slag; ISP smelters can take higher aluminum oxide but are concerned with magnesium oxide content.

Other materials that are treated in lead smelters for lead and other values are scrap lead, scrap batteries, lead ashes and sludges, and zinc smelter leach residues. Metal and battery scrap are the normal feeds for secondary smelters under specific purchase terms. Zinc residues contain substantial lead and silver values in addition to substantial undissolved zinc, and are handled at high cost in additional fuel, fluxes, and slag fuming furnace operation in joint lead-zinc smelters such as the one at Trail.

9.9.2 Lead Statistics

World mine production of lead has been steady at $(3.4\text{--}3.5) \times 10^6$ t/a of contained lead

since the early 1970s. Production since 1925 in millions of tonnes is as follows:

1925	1501	1985	3581
1950	1686	1986	3378
1960	2376	1987	3389
1970	3433	1988	3400
1980	3470		

Table 9.7: World production (primary and secondary) and consumption of refined lead.

Year	Production, $\times 10^6$ t	Consumption, $\times 10^6$ t
1977	5.388	5.466
1985	5.634	5.460
1986	5.464	5.551
1987	5.631	5.623

The estimates of world lead resources shown in Table 9.1 represent a comfortable reserve against expected consumption requirements for the future, and there are excellent prospects for further economic discoveries.

Production (primary and secondary) and consumption of refined lead in the last ten years are shown in Table 9.7, and by area and

Table 9.8: Lead statistics for most important lead producing and consuming countries, 1987 (Source: Metallstatistik 1977–1987).

	Mine production (contained Pb), 10^3 t	Refined production (primary and secondary), 10^3 t	Refined consumption, 10^3 t
Germany	24.5	340.4	344.6
France	2.2	245.5	207.5
Italy	12.2	168.3	244.0
United Kingdom	0.7	347.0	287.5
Former Yugoslavia	82.0	124.6	129.4
Spain	83.2	122.7	105.8
Rest of Europe	156.1	265.4	311.8
<i>Total Europe</i>	<i>360.9</i>	<i>1613.9</i>	<i>1630.6</i>
Japan	27.9	338.5	377.9
Rest of Asia	111.8	244.2	407.3
<i>Total Asia</i>	<i>139.7</i>	<i>582.7</i>	<i>785.2</i>
Africa	214.6	159.9	111.4
United States	318.3	1027.9	1202.8
Canada	413.4	225.8	102.9
Mexico	177.1	185.1	99.6
Peru	192.0	70.8	21.9
Other South America	73.4	140.7	162.6
<i>Total America</i>	<i>1174.2</i>	<i>1650.3</i>	<i>1589.8</i>
Australia, Oceania	186.2	220.7	65.0
<i>Total Western World</i>	<i>2375.6</i>	<i>4227.5</i>	<i>4182.0</i>
Former Soviet Union	510.0	780.0	775.0
Other Eastern Bloc	503.7	623.9	665.5
<i>Total Eastern Bloc</i>	<i>1013.7</i>	<i>1403.9</i>	<i>1440.5</i>
<i>Total World</i>	<i>3389.3</i>	<i>5631.4</i>	<i>5622.5</i>

trading bloc for 1987 in Table 9.8. About one-third of current refined lead production is from recycled materials.

Lead ranked first in production among non-ferrous metals in the first quarter of the twentieth century, but now ranks fourth after aluminum, copper, and zinc. This is due more to consumption growth for the other metals than to decline in lead use. Lead has suffered the loss of some major markets in pigments, water piping, and lead alkyls caused by legislation reflecting concern for its toxicity and environmental impact, from substitutions by plastics and aluminum, and the decrease in requirement for type metal. These losses now appear to have stabilized. They have been more than offset by the growth in production of lead batteries for automobile and transport use. The lead battery represents the dominant use of production and recycled lead and is the mainstay of the lead industry.

Of very considerable concern to the industry has been the slump in lead price, which reflects but far transcends the worldwide industrial recession in the first half of the 1980s (Table 9.9). The price of lead reached its lowest point in recorded history in terms of the real value of money in 1985. The period from 1982 to 1986 saw dismally inadequate returns and outright losses, with the abandonment of many producing mines and severe retrenchment or closure of smelting plants. Since the mid 1980s the price of lead has recovered by over 50%. This has encouraged many lead producers to modernize or replace old smelting plants by the new flash-smelting technologies that are better able to meet the stringent hygiene and environmental regulations that govern plant operation.

Table 9.9: Annual average producer price of lead in the United States (Source: Metallstatistik 1977–1987).

Year	Price (U.S. cents/kg)
1978	74.28
1979	116.20
1980	93.73
1981	80.57
1982	56.38
1983	47.86
1984	56.40
1985	42.10
1986	48.74
1987	79.20
1988	81.08

9.10 Toxicology and Occupational Health

Lead is one of the seven metals used in antiquity by the Euroasian civilization. Its uses were varied. Physicians prescribed various forms of lead to heal ailments ranging from constipation to infectious diseases such as the plague. Lead was also used to preserve or sweeten wine, for water pipes, cosmetics, and ceramic glazes.

The symptoms of lead poisoning have been recognized for centuries. HIPPOCRATES described lead colic in 370 B.C. and PLINY reported poisoning among lead workers in about

50 A.D. In 1700 RAMAZZINI [36] noted the illness of potters who worked with lead. In 1933 KEHOE and his coworkers [37], brought to light the important consideration that lead is very widely found in the environment. Their studies showed that although lead is not an essential element for the body, a measurable amount exists in all adult body tissues and fluids.

Today, there is considerable literature on the effects of lead, ranging from overt signs and symptoms of lead poisoning to subtle effects such as reduced intelligence quotient scores, behavioral effects, and impaired hearing. The relevance of these effects and the definition of lead exposure levels are subjects of extensive debate.

9.10.1 Sources of Lead Exposure

Many sources of lead exposure affect the workplace and the general population.

Drinking Water. Drinking water can be a significant contribution to lead intake, especially for young children.

Lead can enter the aquatic system through fallout and surface runoff, from natural sources or from lead-lined tanks, lead pipes, and lead solder joints.

The lead content of drinking water is controlled in the European Economic Community (EEC) and North America by water quality standards, and is subject to revision. The EEC [38] specifies 50 $\mu\text{g/L}$ as a maximum allowable lead concentration in water for human consumption; the Environmental Protection Agency (EPA) of the United States is contemplating lowering its current lead-in-water standards from 50 to 5 $\mu\text{g/L}$ [39].

Lead concentrations in drinking water exceeding 300 $\mu\text{g/L}$ have been reported [40]. Such high contents can be attributed to very soft water, low pH, and high temperature; for example, samples of soft, hot or stagnant 'first draw' water exposed to lead or lead in pipes usually have a high lead content.

Atmosphere. Worldwide natural lead emissions to the atmosphere from natural sources

have been estimated to be 24×10^3 t/a, compared to $(350-450) \times 10^3$ t/a from anthropogenic sources. By far the greatest contribution comes from automotive lead emissions. A determined effort has been made in most countries to reduce the amount of allowable lead in gasoline. The EEC currently stipulates a limit of 0.15 g/L for added lead (the lead is added as tetraethyl lead). A more stringent position has been taken by the United States, where the EPA regulated lead content in gasoline at 0.29 g/L in 1982 and then to 0.026 g/L in 1986.

The lowering of lead in gasoline has been cited by the Center for Disease Control (CDC) in the United States as the major reason for the 37% decrease in children's blood lead levels, based on a nation-wide survey conducted between 1976 and 1980 [42]. Another view is that the effect is attributable mainly to socioeconomic improvements.

Lead emissions from industrial sites such as smelters and metal recovery operations also contribute to atmospheric lead. However, fallout from these sources is localized and is estimated to contribute only about 10% of the overall lead emission. Ambient lead levels in the proximity of primary and secondary smelters can be significant. At El Paso, Texas, mean lead levels in 1971 ranged from 0.46–2.72 $\mu\text{g}/\text{m}^3$ with peak values as high as 22 $\mu\text{g}/\text{m}^3$ [43]. Sampling data from Yugoslavia recorded peak levels in excess of 200 $\mu\text{g}/\text{m}^3$ [44]. Typical levels near point source areas are 0.1–1 $\mu\text{g}/\text{m}^3$ and for rural areas ≤ 0.1 $\mu\text{g}/\text{m}^3$. Community air quality criteria are set in the range of 1.5–2.0 $\mu\text{g}/\text{m}^3$ with a view to lowering these levels. For example, EPA is proposing tightening their current standard from 1.5 $\mu\text{g}/\text{m}^3$ standard to 0.5 $\mu\text{g}/\text{m}^3$.

Soil. Natural soil can contain from 2 to 200 ppm and can be greatly influenced by anthropogenic sources. There are few standards for lead in soil; however, many countries have guidelines with suggested maximum levels of ca. 500–1000 ppm.

Lead-bearing dust can be especially dangerous to very young children because of a high level of ingestion through their play and

eating habits. The concentration of lead in street dust and surface soil can be very high, especially if located near a major freeway. Soil samples from areas of Vancouver, Canada taken near heavy traffic areas were similar to samples taken 1.6 km from a large primary lead smelter complex (1545 and 1662 ppm, respectively) [45]. A survey of street dust in 77 midwestern U.S. cities showed a mean lead content of 1600 ppm in residential areas and 2400 ppm in industrial areas [46].

Diet. Lead (mainly organic compounds) can enter the human body through the skin, by inhalation, or by ingestion. Ingestion in food is generally the major source of lead intake. Lead in the diet can come from numerous sources such as uptake of lead into plants; deposition onto vegetables; from soil or water; and from lead solder in canned goods.

Absorption of lead from the gastrointestinal tract by adults is estimated to be about 5–10%, but 25–55% by young children [47]. Ingestion of lead-based paint by children is still considered the most frequent cause of lead intoxication in the United States [48]. The amount of lead absorbed through the digestive system is greatly influenced by stress, fasting, and the solubility of the lead compound; for example, lead acetate is 25 times more soluble in intestinal fluid than lead sulfide [49].

Occupational Exposure. Workers employed in primary and secondary lead smelters, as well as in the production of lead metal and lead compounds are exposed to lead absorption hazards. Because of the fine particle size of lead fume and its solubility, it can readily enter the respiratory system and be absorbed in the blood stream.

The workplace lead standard in the EEC and North America have been tightened to the current range of 0.05–0.15 mg/m^3 . The MAK value is 0.1 mg/m^3 and the TLV-TWA value is 0.15 mg/m^3 . This has been strong motivation for the development of new process technology, improvement of engineering controls, and stricter use of personal protective equipment by industry to reduce worker exposure.

9.10.2 Absorption and Excretion

Absorption of lead into the body is greatly affected by the size of the lead-containing particle and its solubility.

Retention through the respiratory system is 20–60% [50]. Particles of 0.1–1 μm are small enough to reach the alveoli where absorption into the blood stream can take place; particles larger than 1–2 μm may be deposited in the naso-pharyngeal area, trachea, or bronchi and leave by swallowing or expectoration. Thus, fine lead fume has a much greater influence on a worker's blood lead value than coarser dust.

Gastrointestinal absorption of lead has been discussed earlier. Absorption through the skin is not considered to be important for inorganic lead compounds, but organic lead compounds such as tetraethyl lead or lead naphthenate are readily absorbed across the skin barrier.

Approximately 90% of ingested lead is not absorbed and eliminated in the feces. Lead absorbed into the blood stream deposits to soft tissue and gradually accumulates in bone. Some is excreted in urine. With consistent intake of lead, a steady state between lead concentrations in blood, soft tissue and bone is established [51].

9.10.3 Effects

Acute Effects. The total average daily lead intake for adults is estimated to be 150–300 μg , which is reflected in a blood lead level of 10–25 $\mu\text{g}/\text{dL}$. Blood taken from 'normal' persons in 16 countries in the 1960s showed an average of 17 $\mu\text{g}/\text{dL}$.

Hematological Effects. One of the more deleterious effects of lead is on blood and blood-forming tissue. Lead can inhibit almost all steps in the biosynthesis of hemoglobin and globulin [52].

Neurological Effects. In the early part of this century, excessive prolonged exposure to lead was reflected in brain disease and muscle weakness in lead workers and children. These extreme exposures have long been eliminated.

Today the greatest concerns relate to neurological effects on young children. Neurobe-

havioral deficits have been correlated with lead content in teeth [53], and blood lead levels in children, which were formerly considered to be acceptable, are now being reviewed in many countries. In the United States the tolerable maximum blood lead in children was reduced from 40 to 25 $\mu\text{g}/\text{dL}$ in 1985.

Renal Effects. The kidney is the major route for the excretion of lead that has been absorbed into the body, and it is also one of the organs affected by lead toxicity [54]. In most situations renal dysfunction occurring as a result of chronic lead exposure is reversible provided serious tissue damage has not occurred. However, irreversible renal damage may result from a prolonged, very high lead body burden. Hypertension can also follow.

Reproduction Effects. Toxic levels of lead can cause sterility in men, and miscarriages and spontaneous abortions in women. The fetus is especially vulnerable because lead can cross the placental barrier. Men with blood lead levels $> 60-70$ $\mu\text{g}/\text{dL}$ may have reduced sperm count and mobility [55], but data are not conclusive.

Carcinogenicity. Lead and its compounds are currently under close scrutiny by the EPA with respect to its potential as a cancer-causing agent. The international Agency for Research on Cancer has listed inorganic lead compounds in Group 2B (agents that are possibly carcinogenic to humans), but this is a wide generalization from observations limited to lead acetate and phosphate [56].

9.10.4 Indices for Monitoring Lead Exposure

Biological monitoring of workers provides an assessment of overall exposure to a chemical or compound, and sets guidelines for the evaluation of potential health hazards. Several of the more common indices for evaluation of overall lead absorption are outlined below.

Lead in Blood. Lead in blood is generally considered the best indicator of the lead con-

centration in soft tissue and is an effective means of assessing exposure to lead. Some investigators have been able to predict increases in blood lead after low lead exposures with some accuracy [57]. Blood lead levels of 60–70 µg/dL in male workers have generally been considered acceptable [58], but some authorities such as OSHA have established a limit of 50 µg/dL, and the World Health Organization is proposing an upper limit of 40 µg/dL for males and 30 µg/dL for females.

Lead in Urine. Lead in urine best reflects a sudden, recent exposure and is a sharper index than the subsequent, more gradual change in blood lead concentration. Although correlation between blood and urinary lead levels is often poor, under stable conditions a urinary lead value of 150 µg per gram of creatinine corresponds to a blood lead of 60 µg/dL.

Urinary ALA. Urinary δ -aminolevulinic acid (ALA) found considerable success as a means of screening suspected lead intoxication or lead poisoning in the late 1960s and early 1970s. This nonspecific test measures the effect lead has on the hematopoietic system. The analysis is cumbersome and has been gradually replaced by other tests.

Zinc Protoporphyrin. Lead can block normal hematopoiesis by inhibiting the enzyme ferrochelatase and this causes elevation of zinc protoporphyrin (ZPP) in red cells [59]. Assessment of the ratio of ZPP to hemoglobin can be made by measuring ZPP fluorescence. This nonspecific screening test for lead toxicity has been available since the early 1970s.

Teeth and Hair. Lead content in teeth, particularly dentine, has been used to assess exposure and measure psychological deficits in children but is not practical for second-growth teeth. Hair has also been suggested as a method of evaluating lead absorption, but it is almost impossible to discern between intrinsic lead and that absorbed on the surface from external sources.

9.11 Control of Lead Emissions

The adverse effects of lead ingestion on the health of humans and animals make control of lead emissions a major operating challenge in all primary, secondary, and processing production industries. This overall problem has a dual focus:

- The effect of emissions on in-plant atmospheric contamination and lead absorption by production workers.
- The effect of plant emissions on ambient air lead levels and accumulative lead dust fallout on areas around the production site.

This challenge has long been part of the lead production industry, but since the 1970s improved diagnosis of biological problems related to lead and the resulting increased government regulatory pressure have greatly increased the demand for reduction of overall emission. Improved engineering controls and total process revisions are the broad approaches that have been taken to achieve compliance. Much progress has been made worldwide; however, the degree of success largely depends on the regulatory standards which have been set or proposed. In the United States, the proposed levels of 50 µg/m³ for in-plant air and an annual mean of 1.5 µg/m³ for lead in air outside the plant boundaries represent perhaps the most difficult industrial challenge.

9.11.1 In-Plant Lead Emissions

Engineering Controls. Assuming major process gas flows are handled by efficient dust removal equipment and discharged in high stacks, in-plant lead levels are mainly influenced by fugitive process emissions. Well-engineered ventilation systems are required to control dust and fume emissions from hot sinter or molten slags. The provision of effective ventilation is costly in terms of energy usage and capital cost.

Personal Respirators. The use of personal respirators by plant workers is almost univer-

sal practise to reduce respiratory lead intake from the plant atmosphere. The use of respirators is often construed as evidence of inadequate engineering control of fugitive emissions. Certainly the elimination of respirator use for most production jobs other than special maintenance work is a desirable objective, but, it is not being achieved in most plants at present. Personal hygiene habits are increasingly recognized as critical to controlling lead intake by workers. Measures such as provision of clean clothing, compulsory washing, no smoking or eating on the job, and clean eating facilities are common.

Process Revisions. The new oxygen smelting processes described in Section 9.5.4 are attractive because they have inherent advantages for lead emission control. The traditional sintering and blast furnace method of lead production is a most difficult engineering challenge for achieving good control of in-plant emissions. The sinter operation involves large recirculating flows of hot, dusty, abrasive sinter requiring large ventilation volumes. Blast furnace reduction can be an erratic operation often troubled by a hot top and blowing and accompanying fugitive emissions from the gas collection system.

The new oxygen smelting processes have the following favorable characteristics:

- Inherent lower process gas volume with oxygen usage giving less cleaning and reduced emissions
- Recirculating loads requiring separate ventilation are minimized
- Equipment is relatively compact and well sealed

The introduction of these new pyrometallurgical processes over the next one to two decades should have a major beneficial impact on the in-plant and ambient lead emission problems of today's primary lead smelters.

9.11.2 Ambient Lead Emissions

Ambient lead emissions originate from residual lead after cleaning of process and ventilation gas and general fugitive lead emissions.

The accumulation of ambient lead fallout on vegetation eaten by cattle or the buildup of an objectional concentration of lead in the top soil is the most serious aspect of ambient emissions. The current use of high-efficiency baghouses for cleaning process and ventilation gases, combined with curtailment of fugitive emissions of dust and fume from process equipment, roads, and stock yards, have made major reductions in ambient emissions at most primary and secondary lead smelters.

9.12 Alloys

Lead is one of the oldest known metals. Its use was known before 3000 B.C. All early civilizations used lead extensively for ornamental and structural uses. The use of lead pipes for the transportation of water by the Romans, one of the early uses of lead, endures to the present.

The primary and most important mineral for recovery of lead is galena, PbS. Lead ores are found on every continent, usually in combination with zinc, copper, and silver. The United States is the leading lead-producing country followed by Canada and Australia. Total annual production of lead and lead alloys in 1987 was about 4.3×10^6 t. Recycling of lead scrap, mainly from batteries, lead sheet, and cable sheathing, provided 2.1×10^6 t.

About 40% of lead is used as pure lead, lead oxides, or lead chemicals; the remainder is used in the form of lead alloys. The major uses of lead alloys are: lead acid batteries, ammunition, cable sheathing, building construction (sheets, pipes, and solders), bearings, gaskets, specialty castings, anodes, fusible alloys, shielding, and weights.

Lead is a heavy, soft, bluish gray metal which has a low melting point and a high boiling point. The density, malleability, lubricity, flexibility, and coefficient of thermal expansion are quite high. The elastic modulus, elastic limit, tensile and compression strength, hardness, and electrical conductivity are relatively low. Lead has excellent resistance to

corrosion in a wide variety of media. Lead is easily alloyed with many other metals. Because lead alloys have low melting points, they can be cast into many shapes by using a variety of molding materials and casting processes.

Lead is very ductile and malleable, and can be fabricated into various shapes by rolling, extruding, forging, spinning, and hammering. The low tensile strength and very low creep strength of lead make it unsuitable for use without the addition of alloying elements. The major alloying elements used to strengthen lead are antimony, calcium, tin, copper, tellurium, arsenic, and silver. Minor alloying elements are selenium, sulfur, bismuth, cadmium, indium, aluminum, and strontium.

9.13 Compounds

Lead is one of the oldest known metals, dating from about 3000 B.C. The Romans used lead extensively for water pipes, while in ancient Egypt, lead compounds were employed for glazing pottery and ornamental objects, a purpose for which they are still used today. Now, the largest single use of lead compounds, mainly lead oxide, is for the manufacture of lead acid storage batteries. Other industrially important uses of lead compounds range from antiknock additives in gasoline to lead crystal glasses and stabilizers for plastics during thermal processing.

9.13.1 Salts and Oxides

Lead is an amphoteric element, which forms lead salts with acids as well as metal salts of plumbic acid with alkalies. Lead forms many salts, oxides, and organometallic compounds. Although lead has four electrons in its outer (or valence) shell, the usual valence of lead is 2+, rather than 4+, because of the reluctance of its two 6s electrons to ionize. Also, the divalent plumbous ion differs from the other group 14 divalent ions, such as the stannous ion (Sn^{2+}), in that it does not have reducing properties.

Many inorganic lead compounds have two or more crystalline forms with different properties. As a result, the oxides and sulfide of divalent lead often appear colored because of their state of crystallization. Thus, pure, tetragonal α -PbO is red; orthorhombic β -PbO is yellow; and crystals of lead sulfide, PbS, have a black, metallic luster. On the other hand, the carbonates, sulfates, nitrates, and halides (except for the yellow iodide) are colorless.

Highly crystalline basic lead salts, both anhydrous and hydrated, are readily formed. For example, tetrabasic lead sulfate, $4\text{PbO} \cdot \text{PbSO}_4$, and the tribasic lead sulfate hydrate, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, are prepared by boiling suspensions of lead oxide and lead sulfate in water. Moreover, complex mixed salts, such as white lead, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, are readily formed.

Most lead compounds are derived from pig lead (refined metal), usually via conversion to lead monoxide (PbO), commonly known as litharge. In general, lead compounds may be formed by the reaction of a slurry of litharge and the appropriate acid, by the reaction of a solution of a lead salt with an acid, or by fusion of litharge with the appropriate metal oxide. In the latter case, for example, the ease with which lead monoxide combines with silicon dioxide to form a low-melting silicate has been utilized in the ceramics industry for producing glasses and glazes.

9.13.1.1 Acetates

Lead reacts readily with acetic acid to form four different lead acetate compounds: anhydrous, basic, trihydrate, and tetraacetate. Some physical properties of the lead acetates are summarized in Table 9.10.

Anhydrous lead acetate, plumbous acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is a white, crystalline solid that is very soluble in water. It is made by dissolving lead monoxide or lead carbonate in concentrated acetic acid. Solutions of lead acetate are often used to prepare other lead salts.

Table 9.10: Physical properties of lead acetates [67].

Compound	mp, °C	ρ , g/cm ³	Solubility, g/100 mL H ₂ O (t, °C)
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	280	3.25	44.3 (20), 221 (50)
$2\text{Pb}(\text{OH})_2 \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	75 (dec. 200)		6.25 (15), 25 (100)
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	75 (dec. 200)	2.55	45.6 (15), 200 (100)
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	175	2.228	dec.

Basic lead acetate, lead subacetate, $2\text{Pb}(\text{OH})_2 \cdot \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, is a heavy white powder that is very soluble in water and soluble in ethanol. It is prepared by dissolving lead monoxide in dilute acetic acid. Basic lead acetate is used for sugar analysis.

Lead acetate trihydrate, sugar of lead, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, is a white, monoclinic crystalline solid having a refractive index (along the β axis) of 1.567. It is very soluble in water, but insoluble in ethanol. Lead acetate trihydrate is prepared by dissolving lead monoxide in hot dilute acetic acid; large, long crystals separate upon cooling. Although the crystals are intensely sweet, they are poisonous. Lead acetate trihydrate is the usual commercial form of lead acetate and it is available in technical and reagent grades. It is used to make other lead compounds (for example, basic lead carbonate, lead chromate, and lead salts of higher fatty acids), as a mordant for cotton dyes, as a water repellent, and as a processing agent in the cosmetic, perfume, and toiletry industries.

Lead tetraacetate, plumbic acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$, is a colorless, monoclinic crystalline solid that is soluble in chloroform and in hot acetic acid, but decomposes in cold water and in ethanol. Lead tetraacetate is prepared by adding warm, anhydrous, glacial acetic acid to red lead (Pb_3O_4) and subsequently cooling the solution. It is available in laboratory quantities as colorless to faintly pink crystals stored under glacial acetic acid. Lead tetraacetate is often used as an oxidizing agent in organic syntheses because it is highly selective in cleaving vicinal glycols. It also readily cleaves α -hydroxy acids, such as ox-

alic acid, at room temperature. Another use is for the introduction of acetoxy groups in organic molecules [68].

9.13.1.2 Carbonates

Lead carbonate, PbCO_3 , ρ 6.6 g/cm³, forms colorless orthorhombic crystals having refractive indices of 1.804, 2.076, and 2.078. It is slightly soluble in cold water (1.1 mg/L at 20 °C), is soluble in acids and alkalies, but is insoluble in aqueous ammonia and ethanol. Lead carbonate is produced by passing carbon dioxide into a cold dilute solution of lead acetate, or by shaking a suspension of a lead salt (less soluble than the carbonate) with ammonium carbonate at low temperature to avoid formation of basic lead carbonate. Lead carbonate is used in the catalytic polymerization of formaldehyde to give high molecular mass crystalline poly(oxyethylene) [69], to improve the bonding of polychloroprene to metals in wire-reinforced hoses [70], as a component of high-pressure lubricating greases [71], and as a lubricant and stabilizer for poly(vinyl chloride) [72].

Basic lead carbonate, white lead, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, ρ 6.14 g/cm³, forms white hexagonal crystals that decompose at 400 °C. It is insoluble in water, slightly soluble in carbonated water, soluble in nitric acid, and insoluble in ethanol. Basic lead carbonate is made by reacting soluble lead acetate with carbon dioxide in the presence of air. It is no longer used as a white hiding pigment in paints because of its toxicity, but it has many other uses. For example, basic lead carbonate is used as a component of ceramic glazes, as a curing agent with peroxides to form improved polyethylene wire insulation [73], as a color-changing component of temperature-sensitive inks [74], as a component of lubricating grease [75], and as a component of weighted nylon-reinforced fish nets made of poly(vinyl chloride) fibers [76].

9.13.1.3 Halides

Lead combines with the halogens to form the corresponding fluoride, chloride, bromide, and iodide. Some physical properties of the lead halides are listed in Table 9.11.

Table 9.11: Physical properties of lead halides [67].

Compound	mp, °C	bp, °C	ρ , g/cm ³	Solubility at 20 °C, g/100 mL H ₂ O
PbF ₂	855	1290	8.24	0.064
PbCl ₂	501	950	5.85	0.99
PbBr ₂	373	916	6.66	0.844
PbI ₂	402	954	6.16	0.063

Lead fluoride, lead difluoride, PbF₂, is a colorless, orthorhombic crystalline compound up to ca. 220 °C, above which it transforms into the cubic form. Lead fluoride dissolves in nitric acid, but is insoluble in acetone and aqueous ammonia. It is prepared by reacting lead hydroxide or lead carbonate with hydrofluoric acid, or by the reaction of lead nitrate with potassium fluoride. Lead fluoride is used in glass sealing disks for IR sensors [77]; in wear resistant automotive shock absorbers [78]; for the electroless deposition of lead [79]; as a flux for brazing of aluminum and its alloys [80]; in optical glass fibers for IR transmission [81]; and in thin-film batteries [82].

Lead chloride, lead dichloride, PbCl₂, forms white orthorhombic needles having refractive indices of 2.199, 2.217, and 2.260. It is slightly soluble in dilute hydrochloric acid and in aqueous ammonia, but is insoluble in ethanol. It is made by reacting lead monoxide or basic lead carbonate with hydrochloric acid, or by treating a solution of lead acetate with hydrochloric acid and allowing the precipitate to settle. Upon heating in air, lead chloride readily forms basic chlorides, for example, PbCl₂·Pb(OH)₂, which is known as Pattinson's lead white, an artist's pigment. Other uses of lead chloride include: a precursor of organolead compounds [83]; seawater-activable batteries [84]; expanding polymer-based mortar [85]; flux for soldering cast iron and cast brass [86]; sound-insulating rubber sealants [87]; corrosion inhibitor for galvanized

steel [88]; and infrared-transmitting glasses for CO₂ lasers [89].

Lead bromide, lead dibromide, PbBr₂, forms white orthorhombic crystals that are slightly soluble in aqueous ammonia, soluble in acids and in aqueous potassium bromide (due to complex formation), but insoluble in ethanol. Lead bromide decomposes slowly when exposed to light and darkens due to the formation of lead. It is prepared by reaction of hydrobromic acid with lead monoxide or lead carbonate. Lead bromide is used industrially as a filler for name-resistant polypropylene [90], in glass optical waveguides for infrared thermometers [91], and for catalysts for producing polyesters [92].

Lead iodide, lead diiodide, PbI₂, forms a powder of yellow hexagonal crystals that dissolve in alkalis and in aqueous potassium iodide, but not in ethanol. Lead iodide is made by reacting a water-soluble lead compound with hydroiodic acid or with a soluble metal iodide. It is readily purified by recrystallization from water. Lead iodide is used in aerosols for cloud seeding to produce rain artificially [93]; for making high-contrast photographic images of laser radiation [94]; for high capacity cathodes in lithium batteries [95]; and in low-temperature thermographic copying materials [96].

9.13.1.4 Oxides

There are two main oxides of lead, lead monoxide (PbO) and lead dioxide (PbO₂), in which it is divalent and tetravalent, respectively. In addition, lead forms a mixed oxide, Pb₃O₄, and a black oxide which normally contains 60–80% lead monoxide, the remainder being finely divided metallic lead. The largest market for lead oxides is in the lead acid battery industry, where lead monoxide is used to prepare the active paste for the electrode grids. The next largest market for lead oxides is the ceramics industry, which employs these compounds for the production of glasses, glazes, and vitreous enamels. Other major markets for lead oxides are the paint and rubber industries.

Another important outlet for lead oxide is for the production of lead salts, particularly those used as heat stabilizers for poly(vinyl chloride) resins, especially basic lead salts. In 1979, the U.S. plastics market consumed ca. 9500 t of lead salts [97]. Because of its electrical and electronic properties, lead oxide is used in the production of capacitors, electrophotographic plates, transducers, and ferromagnetic and ferroelectric materials. Examples of the latter include mixed oxides, such as lead zirconate–lead titanate, and lead metaniobate.

Some physical properties of the lead oxides are given in Table 9.12.

Table 9.12: Physical properties of lead oxides [67].

Compound	Decomp., °C	ρ , g/cm ³
PbO	1472 (bp)	9.53
PbO ₂	290	9.375
Pb ₂ O ₃	370	
Pb ₃ O ₄	500	9.1

Lead monoxide, litharge, PbO, exists in a red-dish alpha form up to 489 °C; it then transforms to a yellow beta form (massicot), which is stable at high temperatures. It has a water solubility of 17 mg/L at 20 °C, and is soluble in nitric acid, alkalis, lead acetate, ammonium chloride, and chlorides of calcium and strontium. In alkalis, it forms the plumbite ion, PbO₂²⁻. Lead oxides are produced industrially by thermal processes in which lead is directly oxidized with air. In the ball-mill process, metallic lead balls are tumbled in air to produce a "leady" oxide, which typically contains 20–35% free lead. The Barton pot process oxidizes droplets of molten lead at ca. 430 °C to produce either litharge or leady litharge.

The principal use of lead monoxide is in the manufacture of pastes for the grids used in lead acid batteries. It is also widely used in optical, electrical, and electronic glasses, as well as in glazes for fine tableware. To render the lead compounds insoluble in foods, the glazes and vitreous enamels are prepared from frits, in which the lead monoxide is converted to lead bisilicate, for example. Litharge is also used in rubber as a vulcanizing agent, in lead

soaps employed as driers in varnishes, in high-temperature lubricants as a neutralizing agent in organic syntheses, as a heat stabilizer in plastics, and as a starting material in the production of pigments [99]. The preparation, properties, and other uses of lead oxide are described in [100]. The consumption of litharge in the United States is summarized in Table 9.13 according to end-use.

Table 9.13: Litharge consumption in the United States [98].

Industry	Litharge consumption, t			
	1982	1983	1984	1985
Ceramics	30 980	36 782	37 960	65 413
Chrome pigments	6 591	5 973	4 367	3 794
Paints	3 052	3 256	3 635	3 397
Rubber	787	933	1 016	739
Other	10 267	9 596	9 920	10 590
Total	51 677	56 540	56 898	83 933

Lead dioxide, lead peroxide, plattnerite, PbO₂, is a brownish-black crystalline powder consisting of fine flakes in either the orthorhombic alpha or the tetragonal beta form. Lead dioxide decomposes to lead monoxide when heated above 290 °C. Lead dioxide is practically insoluble in water or alkaline solutions. It dissolves slowly in acetic acid or aqueous ammonium acetate, but more rapidly in hydrochloric acid and in a mixture of nitric acid and hydrogen peroxide. It is produced industrially by the oxidation of red lead (Pb₃O₄) with chlorine in an alkaline slurry. Lead dioxide is electrically conductive and is formed in situ as the active material of the positive plates in lead-acid batteries. Since it is a vigorous oxidizing agent when heated, lead dioxide is used in the manufacture of chemicals, dyes, matches, pyrotechnics, and liquid polysulfide polymers [101]. Other applications of lead dioxide include antifriction compositions for plastic sliding bearings [102], ballistic modifiers in high-energy propellants [103], electrodes for seawater electrolysis [104], filters for desulfurization of waste gases [105], and vulcanizing agents for butyl rubber puncture-sealing layers inside tires [106].

Lead sesquioxide, lead trioxide, Pb_2O_3 , is an amorphous, orange-yellow powder. It is insoluble in cold water, it decomposes in hot water, and in acids it decomposes to the corresponding lead salts and lead dioxide. Lead sesquioxide can be prepared from lead dioxide by hydrothermal dissociation. It is used as a ballistic modifier for high-energy propellants [96], as a cathode material in lithium batteries [107], and as an additive to increase the shattering force of explosives [108].

Red lead, lead tetroxide, minium, Pb_3O_4 , is a brilliant orange-red pigment. It is insoluble in water and ethanol, but dissolves in acetic acid or hot hydrochloric acid. Red lead is manufactured by heating lead monoxide in a reverberatory furnace in the presence of air at 450–500 °C until the desired composition is obtained. It is used as a pigment in anticorrosion paints for steel surfaces and in 1984 accounted for U.S. shipments of 11 236 t [109]. It is also used in lead oxide pastes for tubular lead acid batteries [110], in ballistic modifiers for high-energy propellants [103], in ceramic glazes for porcelain [111], in lubricants for hot pressing metals [112], in radiation-shielding foam coatings in clinical X-ray exposures [113], and in rubber adhesives for roadway joints [114].

9.13.1.5 Silicates

Lead silicates are produced commercially to specific PbO/SiO_2 ratios required by the glass and ceramic, paint, rubber, and plastics industries. Some physical properties of lead silicates are given in Table 9.14.

Table 9.14: Physical properties of lead silicates [115].

Compound	<i>mp</i> , °C	ρ , g/cm ³	n_D^{20}
Lead monosilicate	700–784	6.50–6.65	2.00–2.02
Lead bisilicate	788–816	4.60–4.65	1.72–1.74
Tribasic lead silicate	705–733	7.52	2.20–2.24

Lead monosilicate, lead pyrosilicate, $3\text{PbO} \cdot \text{SiO}_2$, is a white, trigonal crystalline powder. It is insoluble in water and comprises 85% PbO and 15% SiO_2 . Commercial lead monosilicate is produced by dry roasting lead monoxide and silica in the mole ratio 3:2. It provides the most economical method of formulating lead-

bearing glazes for the ceramics industry and it is also used in the glass industry as a source of PbO.

Lead bisilicate, $\text{PbO} \cdot 0.03\text{Al}_2\text{O}_3 \cdot 1.95\text{SiO}_2$, is a pale yellow powder. It is insoluble in water and has the composition of 65% PbO, 1% Al_2O_3 , and 34% SiO_2 . It is available in granular form (10 mesh) and as a ground powder (325 mesh). Lead bisilicate was developed as a low-solubility source of lead in ceramic glazes for foodware, for which its low volatility and high viscosity are equally important.

Tribasic lead silicate, $3\text{PbO} \cdot \text{SiO}_2$, is a red-dish-yellow powder. It is sparingly soluble in water and has the composition of 92% PbO and 8% SiO_2 . It is available in granular form (10 mesh) and as a powder (325 mesh). Tribasic lead silicate has the lowest viscosity of the three commercial lead silicates and it is used primarily by glass and frit producers.

9.13.1.6 Sulfates

Lead forms a normal and several basic sulfates. The most important compound is tribasic lead sulfate because of its extensive use in the plastics industry.

Tribasic lead sulfate, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, ρ 6.9 g/cm³, refractive index 2.1, is a fine white powder. Its water solubility is 26.2 mg/L at 18 °C. Tribasic lead sulfate is made by boiling aqueous suspensions of lead oxide and lead sulfate. The anhydrous compound decomposes at 895 °C [116]. The addition of 2–7% tribasic lead sulfate to flexible and rigid poly(vinyl chloride) provides efficient, long-term, economical heat stability. The compound is easily dispersible, has excellent electrical insulation properties, and is an effective activator for azodicarbonamide blowing agents for vinyl foams.

9.13.1.7 Other Salts

Several salts of lead are used as heat stabilizers in the processing of poly(vinyl chloride), alone or in combination with a basic lead salt, such as tribasic lead sulfate. These

salts include dibasic lead phthalate, basic lead sulfate phthalate, and dibasic lead phosphite. In addition, dibasic lead stearate is sometimes employed as a combination internal lubricant and heat stabilizer in poly(vinyl chloride). Lead diamyl dithiocarbamate has been used as an antioxidant to retard the increase of viscosity and hardness of road asphalts at a loading of 2–6% in paving trials in the United States, Canada, and Australia [117]. Further field trials are underway to test the commercial feasibility and environmental acceptability of lead-stabilized paving asphalts.

9.13.2 Organolead Compounds

Organolead compounds are those containing one or more lead atoms covalently bonded to at least one carbon atom. Unlike the inorganic compounds of lead, nearly all organolead compounds are derived from tetravalent lead. Table 9.15 gives examples of organolead compounds in which from one to four carbon atoms are directly attached to a lead atom.

Table 9.15: Physical properties of lead silicates [115].*

Compound	<i>mp</i> , °C	Uses
$\text{PhPb}(\text{OAc})_3$	102	Polyurethane foam catalyst [119]
$\text{Bu}_2\text{Pb}(\text{OAc})_2$	103	Anthelmintic for tapeworms [120]
$\text{Ph}_3\text{Pb}(\text{OAc})$	205	Toxicant for shipbottom paints [121]
Et_4Pb	–137	Antiknock agent in gasoline [122]

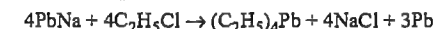
Properties. In general, organolead compounds are well-characterized substances that are quite stable at room temperature. However, they are thermally the least stable of the organometallic compounds of group 14. Most organolead compounds are liable to severe decomposition on heating to 100–200 °C, but they are not explosive. Stable organolead compounds are mostly derived from tetravalent lead and most fall within the four basic categories shown in Table 9.15, namely, RPbX_3 , R_2PbX_2 , R_3PbX , and R_4Pb (where R is an alkyl or aryl group; and X is a halogen, OH, or an acid radical). The R_2Pb species have limited stability and tend to form R_4Pb

upon heating. The tetraorganolead compounds range from the liquid, volatile tetramethyllead, $(\text{CH}_3)_4\text{Pb}$, to the crystalline, nonvolatile tetraaryllead compounds. Some physical properties of tetramethyllead and tetraethyllead are given in Table 9.16.

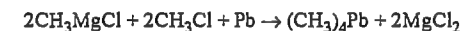
Table 9.16: Physical properties of tetramethyllead and tetraethyllead.

Compound	<i>mp</i> , °C	<i>bp</i> , °C (kPa)	ρ , g/cm ³	n_D
Tetramethyllead	–27.5	110 (101)	1.995 ^a	1.5120
Tetraethyllead	–137	91 (2.53)	1.659	1.5195

Production. The best known industrial process for producing tetramethyllead and tetraethyllead is the reaction of the sodium–lead alloy PbNa with methyl chloride and ethyl chloride, respectively. For example, tetraethyllead is produced according to the reaction:



Tetramethyllead (TML) is also manufactured by an electrolytic Grignard reaction:



In a third lead antiknock production process, a chemically redistributed mixture of tetraalkyllead compounds results. Thus, in the presence of selected Lewis acid catalysts (for example, aluminum halides or boron trifluoride), a mixture of TML and TEL undergoes a redistribution reaction in which an equilibrium mixture of the five possible tetraalkyllead compounds is produced.

Economic Aspects. There are three major industrial producers of TEL and lead alkyl antiknock additives for gasoline: Ethyl Corporation, du Pont, and Associated Octel. Data from the International Lead and Zinc Study Group in London indicate a decline of ca. 66% in the world consumption of refined lead for gasoline additives between 1970 and 1986. Thus, from a peak consumption of 365 200 t in 1970 (excluding Eastern-bloc countries), environmental regulations have resulted in a decline to 124 000 t of refined lead for gasoline additives in 1986 [122]. The limits in 1988 on lead content of gasoline in various countries are given in Table 9.17. These limits were imposed as a means of meeting automotive emission standards. For catalyst-

equipped cars, unleaded gasoline must be used to avoid poisoning of the catalytic converter.

Table 9.17: Limits on lead content of gasoline in 1988 [123].

Country	Maximum lead in gasoline, g/L
United States	0.026
Canada	0.291
Italy, France, Spain, Portugal	0.399
Other EEC countries	0.151
Australia	0.304–0.840
Austria, Sweden, Finland	0.151
Korea	0.301
Venezuela	0.840
Japan	0.000

Uses. Tetraethyllead is used worldwide in gasoline to prevent preignition knock in internal combustion engines prior to completion of the compression stroke. Accordingly, tetraethyllead is commonly called an antiknock agent. This application was for many years the single largest market for organometallic compounds. In addition to providing antiknock qualities to gasolines, organolead additives prevent valve seat wear in engines designed for leaded gasoline.

The preparation and properties of other organolead compounds are described in [118]. Thiomethyl triphenyllead is used as an antifungal agent [124], cotton preservative [125], and lubricant additive [126]; thiopropyl triphenyllead as a rodent repellent [127]; tributyllead acetate as a wood preservative [128] and cotton preservative [129]; tributyllead imidazole as a lubricant additive [130] and cotton preservative [129]; and tributyllead cyanamide and tributyllead cyanoguanidine as lubricant additives [131, 132].

9.13.3 Occupational Health

Lead is toxic in all forms, but to different degrees, depending upon the chemical nature and solubility of the lead compound. In general, organolead compounds are more toxic than inorganic lead salts if ingested, inhaled, or absorbed by humans. Children are more sensitive than adults to the effects of lead exposure. Such exposure may be acute (large

single dose) or chronic (repeated low doses). Prolonged absorption of lead should be avoided because the toxic effects are many, cumulative, and severe.

The most common indications of the onset of lead poisoning (plumbism) are gastrointestinal, including nausea, diarrhea, anorexia, and constipation followed by colic. Since these symptoms of plumbism may be similar to those of other ailments, blood and urine tests should be made on the basis of prior exposure to lead, clinical symptoms, evidence of increased lead absorption, and significant biochemical changes. Lead absorption can affect hemoglobin synthesis, red blood cell survival time, and neuromuscular function. In addition, the toxic effects of lead in women may include decreased fertility, increased abortion, and neonatal morbidity. Encephalopathy is the most serious result of lead poisoning. It occurs frequently in children, when they have very high blood lead levels, but seldom in adults.

Sources of lead in the environment include soils near smelters, lead-pigmented paints, automobile exhaust emissions, food and water, and industrial exposure. Each of these sources is being reduced or eliminated through environmental and occupational safety regulations. For example, in the United States, the ambient airborne lead limit is $1.5 \mu\text{g}/\text{m}^3$, measured over a calendar quarter, which applies to the exterior plant environment and emissions. Moreover, lead-based paints are banned for residential use; leaded gasoline is being phased out; lower limits of lead in drinking water have been proposed (below 20 parts lead per billion parts water).

As a result of exposure monitoring, respiratory protection, protective work clothing and equipment, isolated dining areas, and medical surveillance, there is a very low incidence today of lead poisoning from industrial exposure. Lead-exposed employees in the United States, for example, must be removed from work if the average of their last three blood lead determinations is at or above 50 micrograms lead/100 g whole blood and the airborne lead level is at or above $30 \mu\text{g}/\text{m}^3$ [133]. The permissible exposure limit (OSHA-PEL)

of lead for industrial workers is $50 \mu\text{g}/\text{m}^3$, averaged over an 8 h period. The TLV/TWA for lead is $0.15 \text{ mg}/\text{m}^3$, while the MAK value is $0.1 \text{ mg}/\text{m}^3$. Tetramethyl- and tetraethyllead have an MAK of $0.075 \text{ mg}/\text{m}^3$ ($0.01 \text{ mL}/\text{m}^3$).

9.14 Pigments

9.14.1 Lead Cyanamide

Lead cyanamide, PbCN_2 , is a lemon yellow powder which has the following properties [134]:

Density, g/cm^3	ca. 6.8
Apparent density, g/cm^3	550–750
Metal content, %	ca. 83
CN2 content, %	ca. 16
Specific surface area, m^2/g	2
pH	9–11
Conductivity, μS	< 300

9.14.2 Red Lead

Red lead, Pb_3O_4 , crystallizes in the tetragonal system and is a red powder with a density of $9.1 \text{ g}/\text{cm}^3$. It decomposes at ca. 500°C at atmospheric pressure.

Red lead should be regarded as the lead salt of orthoplumbic acid, H_4PbO_4 , i.e., it is lead(II) orthoplumbate, Pb_2PbO_4 , in which PbO_6 octahedra are linked by Pb(II) ions [135].

Red lead is produced industrially by oxidizing lead monoxide (PbO) at ca. $460\text{--}480^\circ\text{C}$ with agitation in a stream of air for 15–24 h. Most red lead is used in the glass, ceramic, and accumulator industries where an apparent density of $< 2 \text{ g}/\text{mL}$ is adequate. For the paint industry, however, highly dispersed red lead is normally necessary, with a sieve residue of $< 0.1\%$ on a 0.063 mm sieve (ISO 787, Part 18) and an apparent density of $1.3\text{--}2.0 \text{ g}/\text{mL}$ (ISO 510, DIN 55516).

The electrochemical action of red lead results from the fact that lead has valencies of 2 and 4 in lead orthoplumbate: Pb(IV) compounds are reduced to Pb(II) in the cathodic region [136]. The chemical anticorrosive effect is a result of lead soaps that are formed when fatty acids in the binder react with the

red lead. The lead soaps permeate the paint film as lamellae, and give good mechanical strength, water resistance, and adhesion to the steel surface. Furthermore, the corrosion-promoting chloride and sulfate ions are precipitated by lead(II) ions [137].

Red lead is still used for heavy-duty anti-corrosion applications, especially for surfaces bearing residual traces of rust. In waterborne paints, red lead has no advantages over zinc phosphate [138].

A trade name for red lead is Bleimennige, hochdispers (Heubach & Lindgens, Germany).

9.14.3 Calcium Plumbate

Calcium plumbate, Ca_2PbO_4 , density $5.7 \text{ g}/\text{cm}^3$, is a beige powder formed from lead monoxide and calcium oxide at ca. 750°C in a stream of air [139].

The anticorrosive properties of calcium plumbate are inferior to those of red lead [140]. Calcium hydroxide is formed as a hydrolysis product when water penetrates through a primer that contains calcium plumbate. The pH at the metal surface then increases to ca. 11–12 which inhibits corrosion.

The most important use is in primers for zinc-coated substrates. The pH change occurring on hydrolysis of the calcium plumbate etches the zinc surface which improves adhesion of primers, especially on hot-dip galvanized steel [141].

9.14.4 Lead Powder

Lead powder, mp 327.5°C , density $11 \text{ g}/\text{cm}^3$, is a dark gray powder containing 99% metallic lead and ca. 0.5% lead(II) oxide. It is produced by spraying molten lead at ca. 0.5 MPa and sifting. Owing to its high surface area (particle size $1\text{--}15 \mu\text{m}$), it is liable to oxidize, and is therefore supplied in airtight packages or as a paste.

Lead powder can be combined with many binders [142–143]. It does not affect the stability or viscosity of the paint. Binders that absorb only small amounts of water are

particularly suitable (e.g., epoxy resins, chlorinated rubber). When formulating paints based on lead powder, care must be taken not to dilute it with other pigments and extenders by more than 5 vol%.

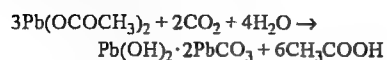
Lead powder coatings are mainly used for protecting against aggressive chemicals. They have a high UV reflection and extremely good elasticity. Lead powder pigments and pastes are also used in radiological protection.

9.14.5 Basic Lead Carbonate

[144–148]

Basic lead carbonate, $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$, is used for white pigments and for nacreous pigments. It is, besides natural pearl essence and bismuth oxychloride, one of the classic pearlescent pigments.

The first commercially successful synthetic nacreous pigments were hexagonal platelet crystals of lead salts: thiosulfate, hydrogenphosphate, hydrogenarsenate, and most important nowadays, basic carbonate. Basic lead carbonate is precipitated from aqueous lead acetate or lead propionate solutions with carbon dioxide:



Under appropriate reaction conditions regular hexagonal platelets (ca. 50 nm thick and 20 μm in diameter) can be obtained. The high refractive index ($n = 2.0$), high aspect ratio (> 200), and the extremely even surface of basic lead carbonate make it an optimal match to natural pearl essence.

The platelet thickness can be adjusted to produce interference colors by modifying reaction conditions. When aligned with its plane orthogonal to the incident light, the platelet crystal behaves as a thin, solid, optical film with two phase-shifted reflections from the upper and lower crystal planes (the phase boundaries).

The crystals are mechanically sensitive and their high density (6.4 g/cm³) results in fast sedimentation. In view of their agglomeration tendency and occupational health (toxic-

ity) risks they are not produced in powder form, but are flushed from the aqueous phase into suitable organic solvents or resins and handled as stabilized dispersions.

Currently, use of basic lead carbonate is limited to artificial pearls, buttons, and bijouterie. Due to the low chemical stability of this pigment and toxicity problems, it is being increasingly replaced by bismuth oxychloride and mica-based pigments. Worldwide production of basic lead carbonate pigment in 1995 was ca. 1000 t.

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10 Zinc

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10.1 History [1, 2, 4, 6–8]

Before 1500 A.D. the Chinese and Indians knew of zinc as a metal in its own right, and although it is not known precisely when zinc was first produced, coins containing 99% zinc were cast during the Ming Dynasty (1368–1644). In a book written in 1637, the Chinese describe zinc production by controlled smelting in stacked, hermetically sealed pots. In India, remains of zinc smelting operations found in Sawai Madhopur (Rajasthan) confirm that

zinc was produced prior to the 1300s. Although the Romans, the Greeks, and the entire western world knew how to produce brass, which was used as early as 8000 B.C. to make jewelry, metallic zinc was unknown. At that time, brass was produced by smelting copper ores or metallic copper with the zinc ore smithsonite. This method lasted until the 1800s. Brass smelting works were developed in the Middle Ages where localized deposits of smithsonite occurred in various places, e.g., near Lüttich and Aachen, and in Carinthia.

The efforts of the alchemists to convert base metals into gold led them to become interested in smithsonite, the ore that gave copper a golden color.

The first written sources to mention the word "zinc" appeared in the 1500s. However, the derivation is not entirely clear. The most likely assumption is that it is connected with the German word *Zinke* (the tooth of a comb), itself derived from *Zacke* (jagged peak), from the jagged appearance of the ore or of deposits in the furnace. A second possibility is that the word is derived from the Persian word *seng* meaning stone. GEORGIUS AGRICOLA (1494–1555), in his important *De re metallica*, describes how a material found in large quantities in the eastern Alps was called "zinc" by the local people. He gave the name "conterfey" to the white substance that was deposited at the front of the smelting furnaces during the treatment of Rammelsberg ores. This often consisted of metallic zinc, although he did not recognize it as such.

The metallurgical properties of zinc were first unambiguously described in Europe when zinc arrived there from India and China after the establishment of trade relations with the Far East.

In 1595, LIBAVIUS investigated a sample of this East Indian zinc imported from Holland and named "calaem". However, he confused it with silver and did not realize that it was the same material as that known as "cadmia" which was scraped off the walls of the furnace when Rammelsberg ore was smelted in the Harz Mountains to obtain lead and silver.

In 1617, LÖHNEYSS also described this process and clearly recognized this metal as "zinc" or the "conterfey" already described by Agricola, used to imitate gold. KUNKEL (1700) and STAHL (1718) considered that smithsonite added a metallic component to the copper during brass production. In 1721, HENKEL produced zinc from smithsonite in Upper Silesia using a process that he kept secret. In 1746, in Berlin, MARGGRAF produced zinc by distilling smithsonite in sealed vessels. He described his production principle in detail, thereby establishing the basic theory of zinc production.

The first industrial production of zinc was carried out in England, where it was produced on a large scale as early as 1720, probably based on knowledge of operating methods used in East Asia. CHAMPION patented a process adapted from brass production to produce zinc by distillation and built the first zinc smelting works in Bristol in 1743, with a capacity of > 200 t/a zinc. He also patented the process for producing zinc from sulfidic ores after preliminary roasting. The English zinc industry is concentrated in Bristol and Swansea even today.

The German zinc industry was founded by RUBERG. The first zinc smelting works, which used the horizontal retort process developed by him, was built in Wessola in Upper Silesia in 1798. The raw material initially used was zinc galmei, a by-product of lead and silver production. Later, it became possible to produce zinc directly from smithsonite, and easily smelted ore. This was shortly followed by the use of zinc blende, which had first to be converted into the oxidic form by roasting. After this development, other smelting works were soon erected in Silesia near the deposits, in the areas around Lüttich, Belgium and Aachen, Germany and in the Rhineland and Ruhr regions.

In the United States, the rich ore deposits led to rapid growth in zinc production in 1840, so that, by 1907, Germany, which had for long been the world's leading producer of zinc, was left behind.

The ores were often highly intergrown, and ore processing by sorting and flotation methods was started in the early 1920s.

At this time, the electrolytic production of high-purity zinc from sulfuric acid solutions was developed by the Consolidated Mining and Smelting Co. in Trail (Canada) and by the Anaconda Copper Co. in Anaconda, Montana (United States).

An important development in zinc production was achieved in 1930 at the New Jersey Co. in Palmerton (United States). Replacing the individual horizontal retorts by a single vertical retort enabled continuous operation

and also yielded relatively pure zinc (ca. 99.5%).

Statistical data on world production of zinc have been available since 1871. At this time, total production was 121 000 t/a, of which 58 000 t/a was produced in Germany and 45 000 t/a in Belgium. Total production at the turn of the century was 472 000 t/a and in 1913 10⁶ t/a. The earliest use for zinc was to produce brass for the manufacture of jewelry, domestic utensils, and coins.

Zinc castings were first produced on an industrial scale in the 1800s by GEISS (1805–1875). Backed by the building contracting SCHINKEL, the zinc foundry established by Geiss soon became of major importance.

The good resistance of zinc towards atmospheric corrosion soon led to its use in sheet steel production. The possibility of rolling zinc at 100–150 °C was discovered as early as 1805, and the first rolling mill was built in Belgium in 1812 by DONY. More such mills were built in Silesia from 1821 onwards.

Hot-dip galvanizing, the oldest anticorrosion process, was introduced in 1836 in France. This became possible on an industrial scale only after the development of effective processes for cleaning iron and steel surfaces. At first, only small workpieces were zinc coated. Continuous hot-dip galvanizing of semifinished products and wire came later.

10.2 Properties [1, 2, 7–11]

Physical Properties. Some physical properties of zinc are listed below.

Relative atomic mass	65.39
Crystal structure, α -Zn	fcc (diamond type)
β -Zn	tetragonal
Transformation temperature α -Zn \rightleftharpoons β -Zn	286.2 K
Heat of transformation	1966 J/mol
Density of β -Sn at 20 °C	7.286 g/cm ³
at 100 °C	7.32
at 230 °C	7.49
Density of α -Zn at 25 °C	5.765 g/cm ³
Density of liquid zinc at 240 °C	6.993 g/cm ³
at 400 °C	6.879
at 800 °C	6.611
at 1100 °C	6.484
mp	505.6 K
Heat of melting	7029 J/mol
bp	2876 K

Heat of vaporization	295.8 kJ/mol
Vapor pressure at 1100 K	9.8×10^{-6} mbar
at 1800 K	7.5
at 2100 K	83.9
at 2400 K	512.0
Thermal conductivity of β -Zn at 0 °C	0.63 Wcm ⁻¹ K ⁻¹
Electrical resistivity of α -Zn at 0 °C	$5 \times 10^{-6} \Omega\text{m}$
β -Zn at 25 °C	11.15×10^{-6}
Superconductivity critical temperature	3.70 K

The remarkably low boiling point of 906 °C (STP) is important in pyrometallurgical zinc production processes. Zinc can be worked at temperatures as low as 120 °C, and its good deformability is the basis for some of its uses.

In the electrochemical series, zinc is more negative than iron. The use of zinc in sacrificial anodes is based on this fact. The important use of zinc to coat iron to protect it from corrosion is based on the formation of passivating protective coatings of basic zinc carbonate by reaction with the atmosphere.

Chemical Properties. Zinc has an oxidation state of 2+ in all its compounds. It forms complexes with ammonia, amines, and cyanide and halide ions. Zinc dissolves in mineral acids, usually with evolution of hydrogen, but in nitric acid with evolution of NO_x. Zinc is used as a strong reducing agent in chemical processes, mainly in the form of powder or granules. Zinc is resistant to air because of the protective coating formed. It is also resistant to halogens, but is rapidly corroded by HCl gas. Because of its high surface area, zinc dust is much more reactive and can even be pyrophoric, e.g., reacting vigorously at elevated temperatures with the elements oxygen, chlorine, and sulfur.

Zinc chloride and sulfate are soluble in water, while the oxide, carbonate, phosphate, silicate, and organic complexes are insoluble or sparingly soluble.

10.3 Starting Materials for Zinc Production [1, 2, 4, 12–15]

10.3.1 Zinc Minerals

With an average concentration in the earth's crust of 65 g/t (0.0065%), zinc is the

24th element in order of abundance. It occurs only in the chemically combined state. Like copper and lead, zinc is a strongly chalcophilic element. It usually occurs as the sulfide, mostly deposited from hydrothermal solutions and simic and sialic magmas. Sedimentary deposits are of less importance. A series of deposits in carbonatic strata shows the characteristics of true marine sedimentary deposits. However, in these cases it can be assumed that the metal was introduced by hydrothermal transport from simic magmas. Zinc deposits, classified according to their origin, are listed here in order of their economic importance:

- Simic vulcanogenic-sedimentary deposits that sometimes occur as massive ore bodies and sometimes as impregnations, e.g., Kidd Creek (Canada), Mt. Isa and Broken Hill (Australia), Anvil Mine (Canada), Bleiberg (Austria), Reocin (Spain), and Rammelsberg and Meggen (Germany). Ores from these deposits represent 60% of total world reserves.
- Simic-hydrothermal or marine sedimentary deposits, e.g., Kipishi (Zaire), Kabwe (Zambia), Tsumed (South-West Africa), and New Zinc Belt and Old and New Lead Belt (United States). Approximately 30% of all ore is produced from these deposits.
- Sialic lodes (impregnation and replacement deposits), e.g., Bad Grund (Germany); western U.S. states such as Idaho, Colorado, and Utah; and Tepca (Yugoslavia). Only 10% of world ore production is from these deposits.

Cadmium, silver, lead, and copper are important by-products of zinc ore extraction. Iso-morphous components of zinc blende such as cadmium, gallium, germanium, indium, and thallium do not form deposits of their own. Some of these metals are recovered during zinc ore processing.

By far the most important zinc mineral today, and probably also the only primary ore, is zinc blende. The other minerals listed here are of only local importance. Native zinc is practically nonexistent.

Zinc blende, sphalerite, ZnS , theoretical composition 67.09% Zn, 32.91% S, is light yellow to black in color, usually black to brown depending on the iron content, crystallizes in the regular tetrahedral system, and has a Mohs hardness of 3–4 and a density of 3.9–4.1 g/cm³.

The most important impurity is FeS, which is always present at concentrations between 0.3 and > 20%. The grades with the highest iron contents are marmatite and christophite. Sulfides of Pb, Cd, Mn, and Cu are often present. Zinc blende also often contains small amounts of As, Sn, Bi, Co, Hg, In, Tl, Ga, and Ge, and nearly always contains Ag and often Au.

Wurzite is the hexagonal modification of ZnS . It often shows a conchoidal or radiating crystalline structure and is therefore also known as conchoidal or radiating blende. Its density is 3.98 g/cm³.

Smithsonite, zinc spar, or calamine, ZnCO_3 , has the theoretical composition 52.14% Zn, 35.10% CO₂. Some of the ZnO can be replaced by FeO, MnO, CaO, or MgO, so that the ZnO content can be as low as 20%. Other typical impurities include SiO₂, Fe₂O₃, and Al₂O₃.

The Mohs hardness is 5 and the density 4.30–4.45 g/cm³. The color is yellowish or reddish to brown, rarely colorless. Smithsonite crystallizes in the trigonal scalenohedral form and is usually amorphous or in amorphous mixtures with other carbonates. Minerals with higher impurity contents include manganese zinc spar (up to 15% MnCO₃), iron zinc spar (up to 53% FeCO₃), copper zinc spar (up to 6% CuCO₃), zinc lead spar (up to 1% PbO), and cadmium zinc spar (up to 7% CdCO₃).

Hemimorphite, $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$, has the theoretical composition 54.30% Zn, 24.94% SiO₂, and 7.4% water of crystallization of which 50% is evolved on heating to 500 °C, the remainder at much higher temperatures.

The color is yellow to brown, more rarely colorless, green, or blue. It forms rhombic pyramidal crystals, but usually occurs in rough, massive, botryoidal, or earthy forms. Its Mohs

hardness is 45 and its density 3.4–3.5 g/cm³. It is often a component of "calamine" ores.

Willemite, Zn_2SiO_4 , has the theoretical composition 58.68% Zn, 26.95% SiO₂. Its color can be white, yellow to reddish, greenish, or rarely blue. It forms rhombohedral crystals, has a Mohs hardness of 5–6 and a density of 4.0–4.2 g/cm³, and can contain FeO and MnO as impurities.

Franklinite, $(\text{Zn}, \text{Fe}, \text{Mn})\text{O} \cdot (\text{Fe}_2, \text{Mn}_2)\text{O}_3$, has the theoretical composition 21% ZnO, 59% Fe₂O₃, 11% FeO, and 8% Mn₂O₃, and can contain SiO₂, Al₂O₃, and MgO as impurities. Its color is black, it is weakly magnetic, and it forms cubic crystals, with Mohs hardness 6.0–6.5, and density 5.0–5.1 g/cm³.

Other zinc minerals of minor metallurgical importance include zinc bloom or hydrozincite, $\text{ZnCO}_3 \cdot n\text{Zn}(\text{OH})_2$; red zinc ore or zincite, ZnO ; and troostite or bainite, $(\text{Zn}, \text{Mn})_2\text{SiO}_4$.

10.3.2 Zinc Reserves

The proven zinc mineral reserves worldwide are estimated at 185.3×10^6 t zinc. Potential reserves amount to 118.1×10^6 t. The undoubtedly considerable Chinese deposits are not included in this estimate, as no concrete information on these is available.

The proven and potential reserves are listed in Table 10.1. Canada, with 37.7×10^6 t (20.3%), has the largest reserves of any country, over 90% of which are in stratified vulcanogenic-sedimentary deposits. North and South America account for over 45.4% of known deposits. Western Europe has 16.7% of world zinc reserves, of which the most important are in Ireland, Sweden, and Yugoslavia (Kosovo). Australia accounts for over 9.5% of world reserves, the largest deposits being in Mt. Isa (Queensland) and Broken Hill (New South Wales).

The most important deposits in the GUS, accounting for 13.2% of the total, are in the central and eastern Kazakh, Uzbek, and Kirghiz. The reserves in Poland (Upper Silesia) are also important.

Table 10.1: The zinc reserves of the world [2, 3, 12, 13].

Country	Proven reserves		Potential reserves	
	10 ⁶ t	%	10 ⁶ t	%
Canada	37 560	20.3	6 620	5.6
United States	31 800	17.1	32 200	27.3
Mexico	3 600	1.9	1 000	0.8
Peru	7 150	3.8	1 500	1.3
Brazil	1 790	1.0	480	0.4
Rest of Latin America	2 360	1.3	2 820	2.4
Africa	5 930	3.2	9 580	8.1
Germany	1 850	1.0	1 500	1.3
Sweden	4 000	2.2	2 000	1.7
Finland	2 000	1.1	1 000	0.8
Ireland	8 820	4.8	350	0.3
Spain	5 060	2.7	1 200	1.0
Italy	2 200	1.2	1 100	0.9
Yugoslavia (Kosovo)	3 500	1.9	2 000	1.7
Rest of Western Europe	3 420	1.8	2 250	1.9
Australia	17 560	9.5	27 950	23.7
Iran	3 700	2.0	1 800	1.5
India	2 650	1.4	3 500	3.0
Japan	9 150	5.0	6 100	5.2
Rest of Asia	1 160	0.6	3 100	2.6
GUS and Eastern Europe	30 000	16.2	10 000	8.5
Total	185 260	100.0	118 050	100.0

10.3.3 Secondary Raw Materials [16, 17]

Typical secondary zinc raw materials include:

- Electric steel plant dusts containing 20–30% zinc (low grade) or 30–40% zinc (high grade)
- Liquor residues from zinc electrolysis containing 25–30% zinc
- Lead shaft furnace slags containing 10–15% zinc
- Residues from thermal zinc production containing 8–12% zinc

Thermal enrichment of such products in the Waelz kiln process gives a Waelz oxide containing 50–58% zinc and 8–12% lead. The lead content can be reduced by calcination. Other sources of secondary raw materials include zinc dross, which is produced in galvanizing plants and has a relatively high zinc content (50–85%); zinc-containing sludges (10–65% zinc), spent catalysts (50–60%

zinc), and dusts from the brass industry (60–75% zinc).

The increasing problems in disposing of zinc-containing materials are resulting in the continual extension of the range of zinc-containing secondary raw materials.

10.4 Pretreatment of Raw Materials for the Production of Zinc Metal [1–4, 10, 18–23]

Pyrometallurgical and electrolytic zinc production require an oxidic raw material. Sulfidic concentrates must be prepared for metal extraction by roasting, which removes the sulfur as SO_2 and converts ZnS to ZnO , but does not remove gangue material.

Low-zinc oxidic ores that are not suitable for mechanical beneficiation (e.g., by flotation), slag flue dusts, and other secondary raw materials are subjected to a thermal concentration stage, which usually consists of either slag fuming or roasting in a Waelz kiln.

10.4.1 Roasting

Both electrolytic and pyrometallurgical zinc production require oxidic raw materials. Sulfidic raw materials must therefore be converted to the oxidic form (known as calcine) before leaching or reduction.

Whereas early accounts of zinc metallurgy listed a large number of roasting processes, fluidized-bed and sinter roasting have now almost completely replaced older processes such as multiple-hearth and flash roasting. An essential requirement of any roasting process is that it must be possible to recover and use the SO_2 from the waste gas.

The various zinc production processes require feed materials with fundamentally different physical properties. A fine-grained calcine is necessary for leaching with dilute sulfuric acid. Flotation concentrates meet this requirement if oxidized by roasting in a fluidized bed. On the other hand, thermal processes require a porous feed material in lump form, as provided by sinter roasting [18].

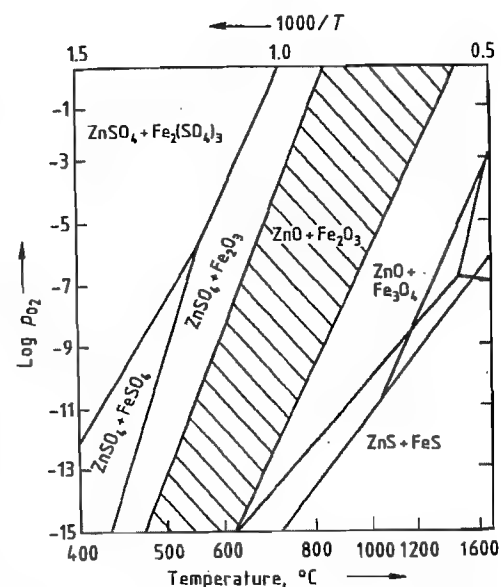


Figure 10.1: Phase diagram of the system Zn-Fe-S-O [23]. The conditions that exist in most fluidized-bed roasters are indicated by the hatched area.

Fluidized-Bed Roasting. Given a processed concentrate of suitable chemical constitution and particle size, the fluidized-bed reactor allows a calcine suitable for the leaching process to be produced. The parameters to be optimized are bed height, gas velocity, residence time, and temperature. In the fluidized-bed reactor, the reaction conditions are easily controlled and stabilized. The theoretical relationships, as shown in the phase diagram Zn-Fe-S-O (Figure 10.1), have been thoroughly investigated [19, 22, 23]. Fluidized-bed roasters generally operate at conditions in which ZnO and Fe_2O_3 are stable. Developments in electrolytic processing technology have enabled the presence of sulfates and ferrites in the calcine to be tolerated.

Fluidized-bed furnaces are often operated in two stages, in the first of which the roasted product contains 6–8% S. This overflows while hot into a second fluidized bed and is roasted with an excess of air to a residual sulfur content of 1.5% [3, p. 662].

Sinter Roasting. The first industrial application of sinter roasting was in the roasting of

lead ore in sintering pans. The crucial development in processing technology came from the sintering of iron ores, the results from which are transferable to the sinter roasting of sulfidic concentrates [21]. It is important that the temperature of the mixture should reach the sintering point. This is determined by the fuel content of the mixture (i.e., in single-stage sinter roasting, by the ratio of concentrate to roasted recycled material), the particle size distribution of the mixture, and the flow resistance (controllable by means of the particle size), which in turn determines the air pressure difference both in the induced-draft and pressure sintering processes. The moisture content of the mixture is an important factor here. It is important that all parameters affecting the process should be kept as constant as possible. Automatic control is not yet widely used.

In contrast to fluidized-bed roasting, where maximum reaction temperatures are in the range 900–950 °C and no volatilization occurs, maximum temperatures in the sintering zone reach 1450 °C, so that the cadmium and lead are volatilized to a considerable extent. For this reason, it is necessary to limit the maximum temperature in the sintering zone.

In principle, the temperatures in the reaction zone during sinter roasting are sufficient to ensure homogeneous sintering not only of concentrates but also of added flue dusts, dross, sludge, and other zinc-containing materials. An important advantage of sinter roasting is thus that it enables these materials to be prepared for shaft furnace treatment continuously and by the shortest route. The important characteristic parameters for sinter roasting, fluidized-bed roasting, and roasting in a multiple hearth furnace are compared in Table 10.2 [3, p. 662].

10.4.2 Pyrometallurgical Concentration Processes

The aim of pyrometallurgical concentration processes is usually the removal of zinc from flue dusts, slags, and low-grade, zinc-containing raw materials or raw materials of complex composition.

Table 10.2: Characteristic values for sinter and fluidized-bed roasting compared with multiple-hearth roasting [3, p. 662].

	Multiple-hearth roaster	Sintering belt	Fluidized-bed roaster
Roasting capacity, $\text{tSm}^{-2}\text{d}^{-1}$	0.08	0.7	7.5
Throughput, t/d	60	500	800
Grain size, mm	1.5	5	3
Dust content, %	13–15	2–3	50
SO_2 in exhaust gas, %	4–5	10	10
Steam output, t/t ore	0.4		1.0
Floor area, m^2td	7	10	3

The Waelz kiln process was originally used for the treatment of low-grade oxidic ores to obtain oxide suitable for smelting [24]. It is now mainly used as an enrichment process to treat secondary raw materials from zinc metallurgy, e.g., slags, flue dusts, and sludges.

In the Waelz kiln process, the zinc and lead from the raw materials appear in the oxide product, together with much of the sulfur, chlorine, and fluorine, both from the raw materials and from the carbonaceous reductant. The zinc metal is usually obtained from the oxide product by a thermal process. For this, the oxide can be compacted by sintering or forming it into briquettes. If oxide with a low lead content is required, it must be calcined, i.e., reheated to 1100–1350 °C without addition of reducing agents, to volatilize the Pb as PbO . The Waelz kiln process is carried out in a slightly inclined, slowly rotating, lined Waelz or rotary kiln through which air is passed at a controlled rate so that the mixture of raw material and coke breeze does not fuse together. The residues are discharged in a sintered but not molten state. Air from the furnace atmosphere diffuses to a limited extent into the reaction mixture which is carried up the walls of the rotating furnace, and a strongly reducing CO/CO_2 atmosphere is formed. This causes reduction not only of ZnO but also of zinc ferrites and silicates, and reoxidation to ZnO occurs after discharge. The following reactions take place in the rotating furnace:

Reaction in the solid charge: $\text{ZnO} + \text{C} \rightarrow \text{Zn}_{(g)} + \text{CO}$

Reaction in the gas space: $\text{Zn}_{(g)} + \text{CO} + \text{O}_2 \rightarrow \text{ZnO} + \text{CO}_2$

The heat liberated is due only to the overall reaction, i.e., the combustion of C to form CO_2 , as the reduction of ZnO to Zn is immediately reversed in the gas space above the charge. The zinc oxide leaving the furnace space is collected in bag filters. As the sulfur and halogens in the waste gases are bound to the zinc oxide, there are no environmental problems. The iron compounds in the charge are reduced to wuestite and to some extent to iron metal. In practical operation, the composition of the reaction mixture must be correctly formulated and an excess of coke breeze must be present to prevent the iron-containing components from fusing and forming incrustations in the furnace. The temperature regime of the process can be controlled by means of the filling height, residence time, and air flow rate in the upper part of the furnace. Overheating can cause incrustations to form and must be prevented [24–27].

Slag Fuming. In contrast to the Waelz kiln method, with which a range of raw materials can be treated, the slag fuming process is only used to remove zinc from molten slags from lead and copper smelting [28]. The zinc oxide so obtained can be used for zinc production. The molten slag is blown with reducing gases, so producing zinc vapor, which is burnt in the gas space above the molten slag by secondary air. The resulting high-grade oxide is cooled in a waste heat boiler in an EGR and collected [3, p. 65]. The composition of the reaction products from slag fuming in Port Pirie (Australia) is given in Table 10.3.

Table 10.3: Composition (in %) of reaction products from a slag fuming plant in Port Pirie, Australia.

	Zn	Pb	CaO	FeO	SiO_2	F	S
Slag before Zn removal	18.3	2.6	14.7	25.6	21.0	0.1	1.7
Slag after Zn removal	2.6	0.03					
Oxide	66.0	12.5				0.25	0.2

Oxide Calcination. The oxides obtained from Waelz kilns or slag fuming plants can be compacted in preparation for further processing by sintering or briquetting, without pretreatment. However, for electrolytic processing, for pig-

ment use, or for production of other zinc compounds, removal of harmful elements such as Pb, Cl, and F is required. This is carried out by calcination in rotary kilns at 1100–1150 °C. Not only are the harmful impurities removed, but the material is also densified [29, 30].

10.5 Production of Zinc Metal [1–5]

There are five industrial processes for the production of zinc: one electrolytic and four pyrometallurgical. Their relative importance during recent decades is illustrated in Figure 10.2 [3, p. 664]. Although the horizontal retort was the most important zinc production process at the turn of the century and still accounted for ca. 50% of total production capacity in 1950, the process is no longer of practical importance. The question of whether the energy-intensive electrolytic zinc production process can retain or even extend its lead depends on the development of the energy supply situation.

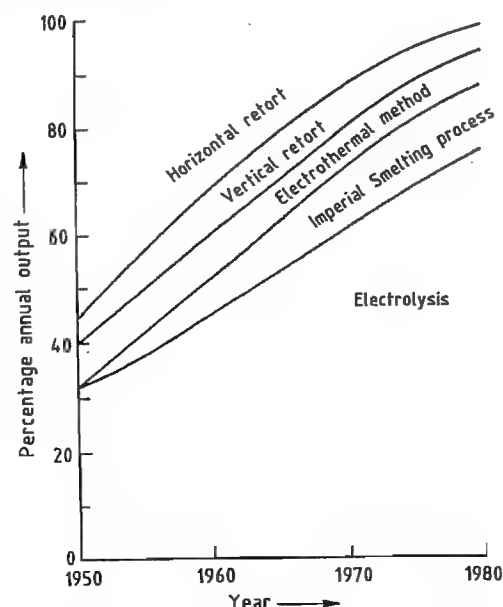
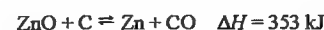


Figure 10.2: Annual outputs of the various zinc production processes expressed as a percentage of total annual output (idealized curves) [3, p. 664].

10.5.1 Pyrometallurgical Zinc Production by the Retort Process

Zinc oxide, produced by roasting, is reduced by carbon according to the equation



The reaction is so strongly endothermic that 5.4 MJ of heat is required to produce 1 kg of zinc. The reaction starts at ca. 1100 °C and is complete at 1300 °C, and the zinc (*bp* 920 °C) is therefore produced as a vapor. Zinc production by the retort process hence involves not only reduction of the oxide but also condensation of the zinc from the vapor to the liquid state. Care must be taken to prevent reoxidation, and the zinc vapor must not come into contact with the combustion gases. The reduction must therefore be carried out either in vessels with exterior heating (retorts) or by the electrothermal method. Horizontal, batch-operated retorts with circular or elliptical cross section can be used, or furnaces containing vertical, continuously operated retorts with a rectangular cross section. The quality of the furnace vessels is of great importance for the process, especially their stability at high temperature, resistance to large temperature fluctuations, good thermal conductivity, impermeability to reaction gases, and resistance towards chemical attack by the charge materials.

Reduction in Horizontal Retorts. Zinc has been produced in horizontal retorts since ca. 1800 in Belgium and Upper Silesia from smithsonite and later from roasted zinc blende. Retorts vary in their shape and arrangement in the furnace and in the fitting of receivers, in which the zinc vapor produced in the retort condenses as a liquid. Detachable devices made of sheet metal (so-called allongen) are fitted to the condensers to collect zinc escaping in the form of dust.

The retort furnaces are equipped with regenerators or recuperators which utilize the hot waste gases to preheat the combustion air and sometimes the fuel gas. The retorts used to be charged by hand, an extremely labor-intensive operation: one worker smelted ca. 0.5 t

ore per shift. Moreover, the yield was poor, only 60% of the zinc being obtained as molten castable metal, 10% remaining unreacted in the ash produced, and the rest reporting to the dross and dust in equal amounts. Although efforts were made to mechanize the process, especially the charging and discharging of the retorts, the main problem, i.e., the poor efficiency (ca. 20%), could not be solved. The horizontal retort is no longer an industrially important zinc production process.

Reduction in Vertical Retorts. The poor efficiency, batch operation, and above all labor intensity of zinc production in horizontal retorts provided the incentive to develop an improved process. The fact that the horizontal retort was inconsistent with the natural downward movement of the charge and upward movement of the zinc vapor suggested that a vertical arrangement would be better. Zinc reduction furnaces were therefore constructed with vertical retorts, but only after overcoming major difficulties. The system is known as the New Jersey process. The furnace, illustrated in Figure 10.3, consists of a retort 13.5 m high, 1.83 m long, and 0.3 m wide, constructed of silicon carbide. The retort is externally heated over a vertical length of 8 m (starting at 1.5 m from the lower end) to a temperature of 1250–1300 °C. Producer gas is fed from above into the heating chambers, and the exhaust gas phases out of the furnace at the bottom. The reaction air is fed through the sides of the furnace along its whole length. Above the heated part of the furnace is an unheated part 4 m in length which acts as a reflux condenser for the lead formed and is known as the lead collector. In the original design, the gas mixture passing out of the retort at 850 °C was cooled to 500 °C by a plate cooler, which also condensed and collected the zinc. This was tapped off from time to time. The zinc dust formed was collected by means of a water spray. The process was much improved by replacing the plate cooler by a spray condenser. A graphite disc, partially immersed in the pool of molten metal and spinning at ca. 400 rpm, atomizes the metal so that the waste gases from the re-

tort passes through a metal fog. The metal is collected at 500 °C in an exterior cooler. This prevents formation of dross, and the amount of zinc dust formed is reduced to 3% of the zinc product.

The charge material, containing 60–70% calcine and 30–40% coal, is formed into briquettes, which are then coked in a coke oven. The coked briquettes are charged into the top of the retort. After extraction of the zinc from the briquettes, they are discharged from the bottom of the retort through a water lute. The zinc-containing gases discharged from the top of the retort are cooled to ca. 500 °C in a condenser, in which the molten zinc collects at the bottom. The tail gases produced, which contain ca. 85% carbon monoxide, are scrubbed and recycled to the producer gas stream. Furnaces with vertical retorts are much more thermally efficient than those with horizontal retorts, and they have the further advantages of providing higher capacity, higher zinc purity, and longer working life of the retorts, and, above all, do not involve heavy manual labor or batch operation.

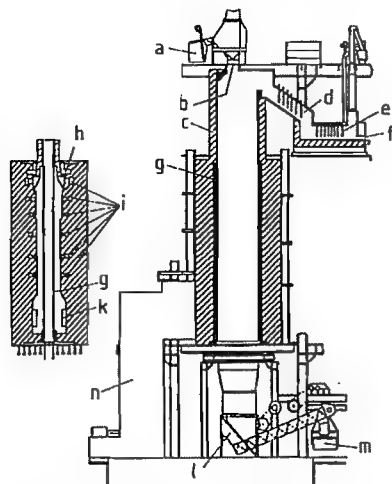


Figure 10.3: Schematic diagram of vertical retort [3, p. 666]: New Jersey retort with plate condenser for zinc recovery. The left- and right-hand sections are rotated 90° with respect to each other. a) Charging bucket; b) Cone; c) Lead collector; d) Inclined channel; e) Condenser; f) Tap hole; g) Retort; h) Fuel gas inlet; i) Air inlets; k) Exhaust gas exit openings; l) Ash removal equipment; m) Ash bucket; n) Recuperator.

10.5.2 Zinc Production in the Shaft Furnace [31]

Prolonged and extensive development work in the 1950s, aimed at utilizing the improved thermal efficiency and higher reaction temperatures of the coke shaft furnace, led to the lead-zinc shaft furnace of the Imperial Smelting Corp. Thus, a process became available that could be used with raw materials of complex composition, such as mixed ores and secondary raw materials containing impurities that would cause severe problems in electrolytic zinc production.

In the shaft furnace, the heat for the reduction is provided by the oxidation of C to CO₂ and CO. Under the reaction conditions normally used in a shaft furnace, the zinc vapor formed would be reoxidized to ZnO by the CO₂ in the furnace gas. Intensive research on the equilibria enabled conditions to be found under which this reoxidation does not occur.

In normal shaft furnace operation, the best possible heat utilization is achieved by using countercurrent flow to heat the charge material. The furnaces are relatively tall, and furnace gas exit temperatures of ca. 200 °C are aimed for. In accordance with the Boudouard equilibrium, this results in higher CO₂ contents in the furnace gas. The zinc shaft furnace requires gas temperatures of 1000 °C. In order not to lower the furnace gas exit temperature by the addition of the cold charge material, the coke is heated to > 800 °C and the calcine is added as hot sinter.

The shaft furnace obtains its heat of reaction from the combustion of coke in the reaction zone. This leads to large amounts of nitrogen in the furnace gas, lowering the partial pressure of the zinc. Therefore, the heat required is generated to a large extent outside the furnace. Thus, the combustion air is preheated to 700–950 °C, enabling the amount of furnace gas to be much reduced. The CO-rich furnace gas is cooled as it passes from the furnace to the condenser. To prevent reoxidation of zinc to ZnO, a small amount of atmospheric oxygen can be added to avoid a temperature

drop. This process step must be carefully controlled.

The zinc collects in a spray condenser. In contrast to the vertical retort process, lead is used as the condensing liquid instead of zinc. Dissolving zinc in lead greatly reduces its activity. As the solubility of zinc in lead is strongly temperature dependent, the zinc can be precipitated by cooling. In practice, a temperature of ca. 550 °C is maintained in the spray condenser. The metal flowing out of the condenser is cooled to 440 °C, causing the zinc to separate from the lead and float on the surface. It then flows over a weir and is collected. As the process does not take place under equilibrium conditions, the recovery of 1 t zinc does not require the theoretically calculated amount of lead (60 t), but ca. 400 t. The zinc is either cast as commercial grade ingots (98.5% Zn) or refined to higher grades.

The first full-scale industrial furnace went into operation in Swansea in 1960. The cross-sectional area of the shaft was 17.2 m², and this remains the standard size even today.

On licensing its ISO process, Imperial Smelting required that licensees should com-

pare their experiences of the process, and this has led to standardization of the major zinc-producing plants and to improvements in the plant performance. For example, the annual output of a furnace with a cross section of 17.2 m² has been increased from 35 000 t zinc and 17 000 t lead in 1963 to 80 000 t zinc and 40 000 t lead in 1990. At the same time the zinc yield was increased from 91.7 to 95.5%, and the lead yield from 94 to 95%. The Pb:Zn ratio in the charge material was increased from 0.49 to 0.6, further enhancing the main advantage of the process, i.e., its ability to treat ores of complex composition. In addition to Zn and Pb, many ores also contain Cu. Most of this is reduced to the metal and dissolved by the lead. Copper contents below 4% give few problems, as the copper separates as dross on cooling the lead and can be removed in the form of a solid crust. Higher concentrations can give problems due to the limited solubility of copper in lead. Special techniques are then required. A schematic diagram of a lead-zinc shaft furnace is given in Figure 10.4.

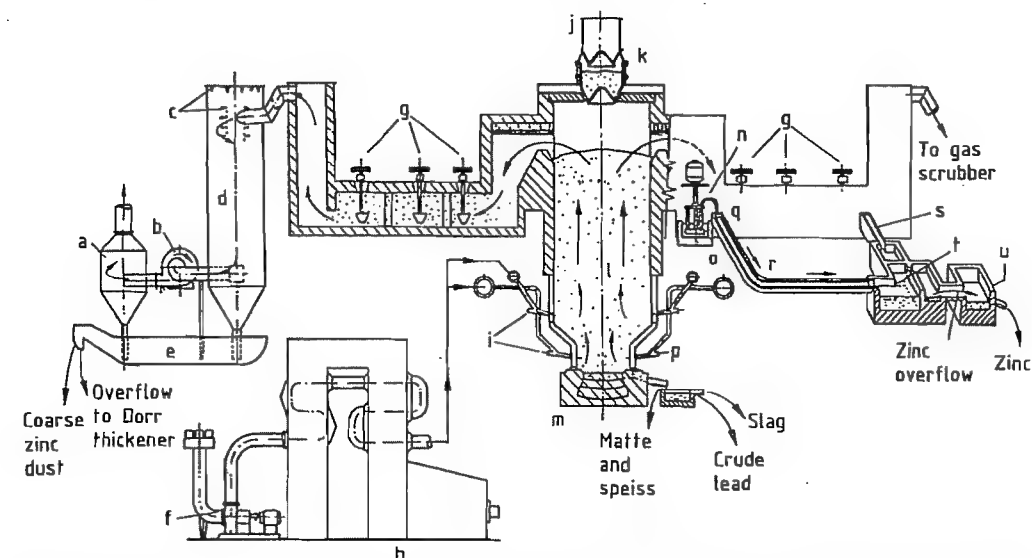


Figure 10.4: Zinc-lead shaft furnace: a) Moisture trap; b) Mechanical washer; c) Water jets; d) Gas scrubbing tower; e) Water seal for zinc dust removal; f) Blower; g) Stirrer; h) Air preheater; i) Jets; j) Feeding vessel for hot coke and calcine; k) Cone; l) Furnace; m) Hearth; n) Lead pump; o) Pump sump; p) Water jacket; q) Condenser; r) Water-cooled trough; s) Lead recycle trough; t) Separating wall; u) Zinc bath.

10.5.3 Refining of Crude Zinc

Zinc produced hydrometallurgically (see Section 10.5.4) does not need to be refined. However, crude zinc produced by pyrometallurgy contains 0.7–3% Pb, up to 0.2% Fe, up to 0.3% Cd, and sometimes small amounts of As, depending on the production method and the composition of the ore. The zinc used to produce pressure casting alloys should have a purity of 99.99–99.995%, and galvanizing processes require a purity of 98.5–99.95%, depending on the process used. Commercial grades of zinc cannot be produced simply by remelting and liquation or by treatment with fluxes. Simply cooling zinc melts until they approach the eutectics in the systems Zn–Pb or Zn–Fe does not produce the theoretical compositions 0.8% Pb and 0.02% Fe, respectively. The concentrations obtained in practice are 1.2% Pb and 0.03% Fe.

Hence, these processes are only suitable for producing zinc for the next stage of purification by distillation or for producing zinc dust. The refining of commercial zinc produced by a pyrometallurgical process (today usually the Imperial Smelting Shaft Furnace process) is carried out by distillation in high-temperature distillation columns constructed of ceramic-bonded SiC elements. The process was developed by the New Jersey Zinc Co., Palmerton (United States), and the first plant went into operation in 1932.

The distillation process makes use of the comparatively low boiling point of zinc (906 °C). However, as not only impurities with a high boiling point such as lead, copper, tin, and iron must be removed, but also cadmium, which boils at 762 °C, the refining process must be carried out in two stages. A plant based on the New Jersey process is illustrated in Figure 10.5. Molten crude zinc is fed into the top third of a distillation column, the lower part being heated to ca. 1100 °C. The upper part acts as a reflux cooler for the less volatile constituents, so that only Zn and Cd pass into the condenser. Because of the relatively small difference in boiling point between zinc and cadmium and the low cadmium content, a fur-

ther very careful fractional distillation must be carried out. The column for this is heated to ca. 950 °C, and the Cd which distills off is collected as a dust with a high zinc content. Depending on the composition of the initial materials and the quality of the process control, the zinc produced can have a purity of 99.996% and the concentration of the desired elements Pb, Cd, and Fe can be < 0.001%.

The “washing” zinc produced in the lead column contains Pb, Fe, Cu, and sometimes also In and Tl. The washing zinc is liquated, giving hard zinc and very impure lead. The hard zinc is recycled to the process, but the lead can be treated separately. In practice, this very impure lead is often added to crude lead from a smelter before it is refined.

The working life of the distillation columns is 2–3 years, and the energy consumption for 1 t of purified zinc is 6.5–7.3 GJ.

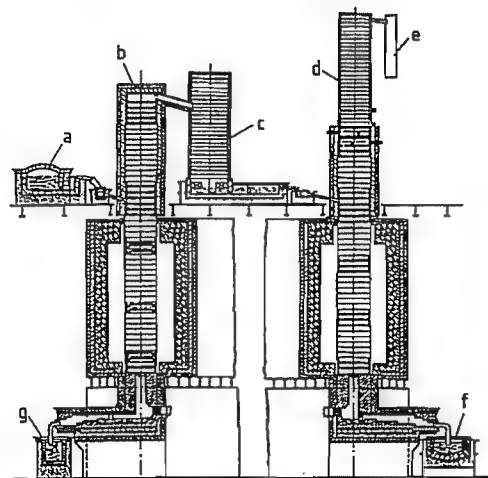


Figure 10.5: Zinc refining plant using the New Jersey process [3, vol. 1a, p. 116, Figure 34]: a) Melting furnace; b) Lead column; c) Condenser; d) Cadmium column; e) Cadmium canister; f) High-purity zinc furnace; g) Washed zinc furnace.

10.5.4 Hydrometallurgical Zinc Production [1–5, 10, 13]

Zinc can be deposited electrolytically both from aqueous solutions and molten salts. However, only aqueous electrolytes (i.e., solutions of zinc sulfate in dilute sulfuric acid)

have so far been used in industry. Other proposed processes such as the electrolytic production of zinc dust, amalgam electrolysis, and sulfate–chloride electrolysis have not attained industrial importance. Although a full-scale version of the electrolytic refining process, in which the impure zinc forms the anode, has been developed, it is not used, the reasons being mainly economic. The electrolytic production (electrowinning) of zinc from solutions of zinc sulfate in sulfuric acid has undergone unparalleled growth in recent decades. Approximately 80% of total world production comes from this process today, although a number of problems still need to be solved, principally in the preparation of pure electrolyte solutions.

Like the thermal processes of zinc production, the industrial electrolysis of zinc uses oxidic starting materials. The most important natural raw material, zinc blende, therefore still needs to be roasted to be converted to oxide. To ensure rapid dissolution of the calcine, the roasting processes used should therefore conserve the fine grained structure of the concentrate obtained by flotation. Commercial zinc oxide can usually be used directly and need only be treated if it contains impurities that have a harmful effect on the electrolytic process. Roasted oxide must be ground to improve its solubility. Using typical starting materials, the electrolytic process of zinc production consists of the following stages (Figure 10.6):

- Roasting
- Leaching
- Liquor purification
- Electrolysis
- Melting and casting.

The main problem in leaching and liquor purification is zinc–iron separation. In earlier processes, leaching was carried out such that a large excess of acid was avoided. Thus, the calcine and acid (exhausted electrolyte) were added simultaneously to the leaching tanks, the amount of acid being exactly that required to dissolve the zinc oxide. High yields of zinc could only be obtained with concentrates con-

taining ≤ 3% Fe. Iron in higher concentrations was dissolved to some extent. The solid residues contained ca. 20% Zn and 30% Fe. However, as a result of the roasting process, part of the zinc in the calcine is in the form of zinc ferrite (ZnFe_2O_4), which can only be dissolved at higher acid concentrations (50–150 g $\text{H}_2\text{SO}_4/\text{L}$). Maximum yields of zinc and also of other valuable impurities such as copper and cadmium require the use of higher acid concentrations in the leaching process. Hence, almost complete dissolution of the iron content of the zinc blende cannot be avoided. As the iron interferes with the electrolytic process even at low concentrations, it must be precipitated from the zinc sulfate solution obtained.

Precipitation of Iron Hydroxide. Precipitation of iron as its hydroxide has now been largely superseded owing to the poor zinc yield obtained (85–88%). The process is usually carried out in two stages.

The readily dissolved zinc oxide fraction is brought into solution by “neutral leaching” in a mixture of cell acid (150–200 g $\text{H}_2\text{SO}_4/\text{L}$) and the acidic solution (ca. 50 g $\text{H}_2\text{SO}_4/\text{L}$) produced during iron precipitation. At this stage of the process, it should be ensured that impurities such as iron, arsenic, antimony, and germanium are retained in the solid residues. A solid–liquid separation is carried out, giving an impure neutral liquor which is fed to the purification stage and a zinc-rich residue which is fed to the second, acid leaching stage, for which hot (ca. 95 °C) cell acid is used. A further solid–liquid separation produces a solid residue containing up to 5% zinc and any lead and silver present (which can be processed in a lead smelter) and a zinc solution containing ca. 80 g/L zinc together with the iron and other impurities, such as arsenic, antimony, germanium, nickel, and cobalt.

After oxidation of Fe(II) to Fe(III) in the solution obtained by “neutral leaching”, the iron is precipitated as its hydroxide by adding further calcine. The precipitation starts at pH 2.6 and continues up to pH 5.0. This gives solutions with residual iron contents of 10–20 mg/L. Because precipitation of iron causes ar-

senic, germanium, and zinc to be adsorptively coprecipitated, and the calcine used for neutralization cannot be subjected to hot acid leaching, this process gives unsatisfactory zinc yields. Higher zinc yields are only possible if the leaching residues can be more readily filtered. Three methods of achieving this are available, i.e., precipitation of the iron as jarosite, goethite, or hematite.

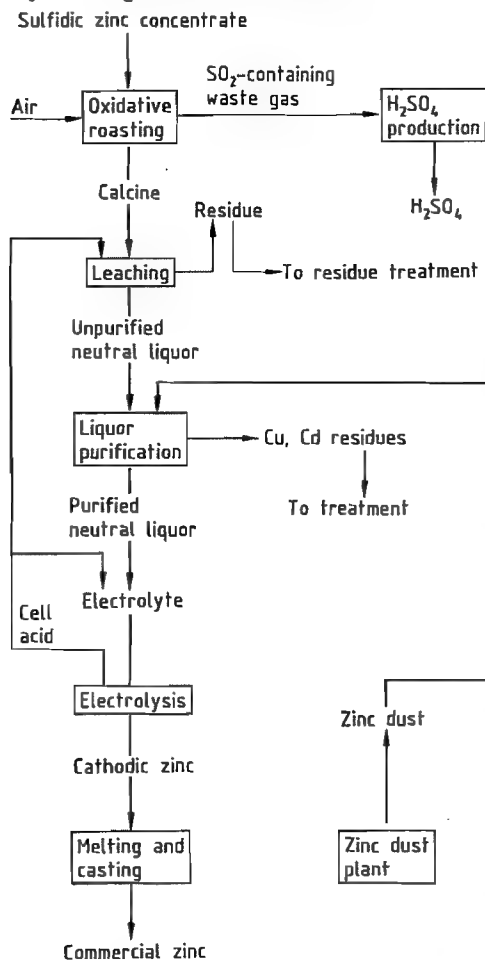


Figure 10.6: Flow diagram of the electrolytic zinc production process [2, p. 602].

Iron Removal by the Jarosite Process. In the jarosite process, an Fe(III) compound of the type $X[Fe_3(SO_4)_2(OH)_6]$, where X represents H_3O^+ , Na, K, or NH_4^+ , is precipitated by adding alkali metal or ammonium ions. These com-

pounds correspond to the mineral jarosite. The process was independently developed between 1960 and 1965 in various zinc smelting plants around the world. It makes use of the fact that jarosite precipitates have the following advantages over iron hydroxide:

- They are almost insoluble in sulfuric acid
- They have a high iron content, so that the amount of precipitate formed is low
- They have good filtering properties

However, jarosite precipitates do not adsorb the harmful impurities as effectively, so that the purification effect of the process is inferior.

The additional cations needed for the precipitation are added to the liquor in the form of sulfates. In practice, ammonium sulfate, which forms an ammonium jarosite, is usually used.

A flow diagram of the process is given in Figure 10.7.

Precipitation of jarosite begins at pH < 1 and is complete at pH 1.5. Jarosite formation and precipitation being a temperature-dependent process, two alternative industrial processes exist, the first operating at temperatures up to 180 °C and with relatively high acid concentrations (60–90 g H_2SO_4/L) giving a high reaction rate, and the second at ca. 95 °C and considerably lower acid concentrations (5–10 g/L). The lower temperature method is more widely used, mainly because of the lower equipment costs.

Jarosite theoretically contains 37% iron and 13% sulfur as sulfate. In practice, these values are not reached, as the calcine added for pH control is not completely dissolved and hence adds impurities to the solid residue. For this reason, additional leaching processes are carried out, giving zinc contents of 4–6% in the residue. Zinc yields of 96–98% can be achieved by the jarosite process. As the jarosite contains sulfate, it helps regulate the sulfate balance of the plant.

Worldwide, the jarosite process has superseded the precipitation of iron hydroxide. However, problems are caused by the fact that the jarosite contains small amounts of soluble

zinc and so must be deposited in special waste disposal sites. New processes aimed at further increasing the zinc yield have therefore been developed.

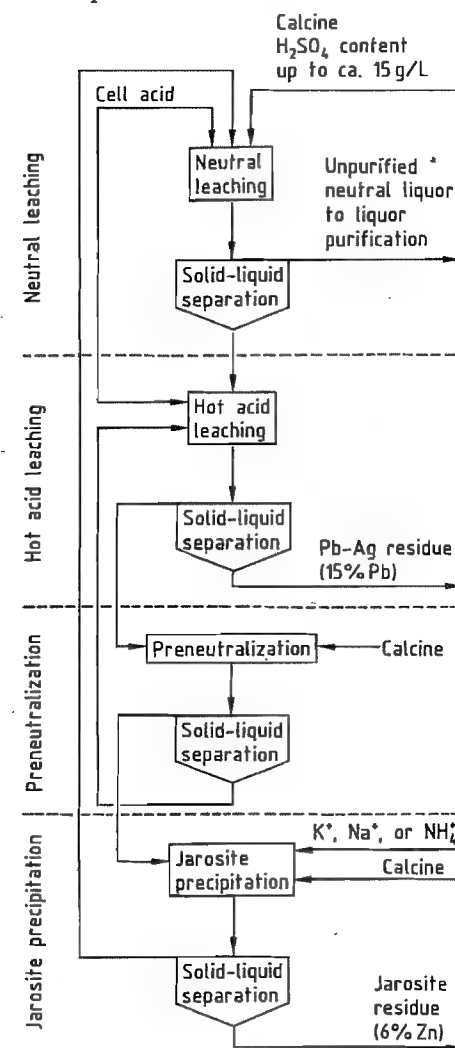


Figure 10.7: Flow diagram of the jarosite process with preneutralization [3, p. 678].

Iron Removal by the Goethite Process. As the flow diagram (Figure 10.8) shows, the first stages of the goethite process are the same as in the jarosite process. The solution from the first hot leach is then treated with zinc concentrate. The zinc dissolves, reducing the iron to the divalent state, and elemental sulfur is pre-

cipitated, so that compounds other than goethite (e.g., jarosite) are not precipitated in the final precipitation process. The excess zinc concentrate and the elemental sulfur are recycled to the roasting process. Oxygen is added in a controlled manner, precipitating goethite, $FeO(OH)$, at pH 2–3.5 and 70–90 °C.

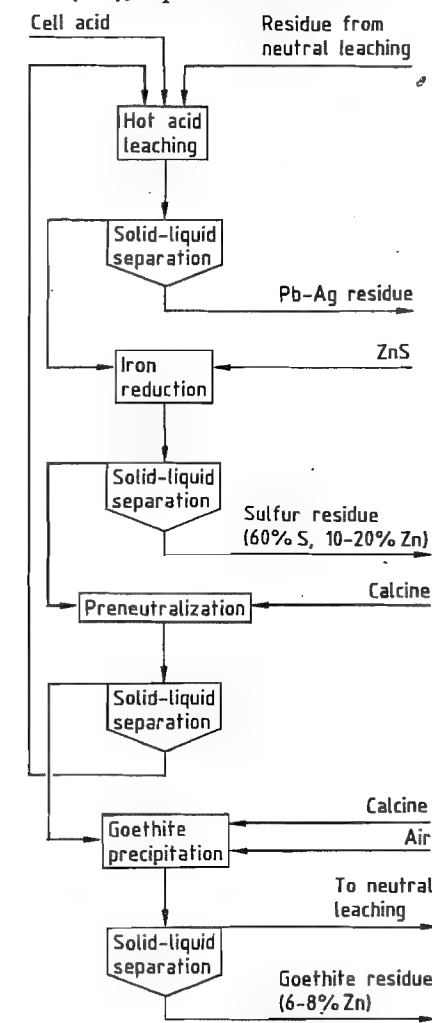


Figure 10.8: Flow diagram of the goethite process [3, p. 679].

The advantage of the goethite process is that the amount of residue that must be disposed of is considerably less than in the jarosite process. Whereas the zinc yield is comparable to the jarosite process, the yield of

copper is lower (80% instead of 90%) and that of silver is higher (96% instead of 90%). As the goethite produced, which contains 40–45% iron, always contains small amounts of basic sulfates, it cannot be used in blast furnaces.

Iron Removal by the Hematite Process. The hematite process (Figure 10.9) was developed to enable iron-containing residues from zinc production to be disposed of at moderate cost and without ecological problems. It differs from the other processes in that the residues are subjected to reductive leaching in which the reducing agent is an excess of zinc concentrate. The iron is reduced with formation of elemental sulfur. The insoluble solids and the liquor are heated in autoclaves, causing the sulfur to melt and wet the excess of zinc blende, forming small pellets. These are cooled, classified, and fed to the roasting plant. A lead–silver residue, which separates from the solution, is sent to a lead smelting plant. The liquor is preneutralized with calcine, and the resulting precipitate is recycled to the hot reductive leaching stage. The copper is precipitated from the zinc–iron solution by addition of zinc (cementation), and the solution is then neutralized with calcium carbonate. This is followed by the most important stage of the process, pressure treatment in an autoclave at 200 °C at an oxygen pressure of 10–15 bar. Under these conditions, iron is precipitated as Fe_2O_3 (hematite), which can be used in iron metallurgy. The zinc solution is recycled to the neutral leaching stage. The gypsum produced is dewatered and can then be used in the building materials industry. The yields of zinc and other valuable metals are comparable to those in the jarosite and goethite processes. As the iron can be produced in the form of a useful product, no landfill space is required. However, the costly and complex technology is restricting more widespread use of the process.

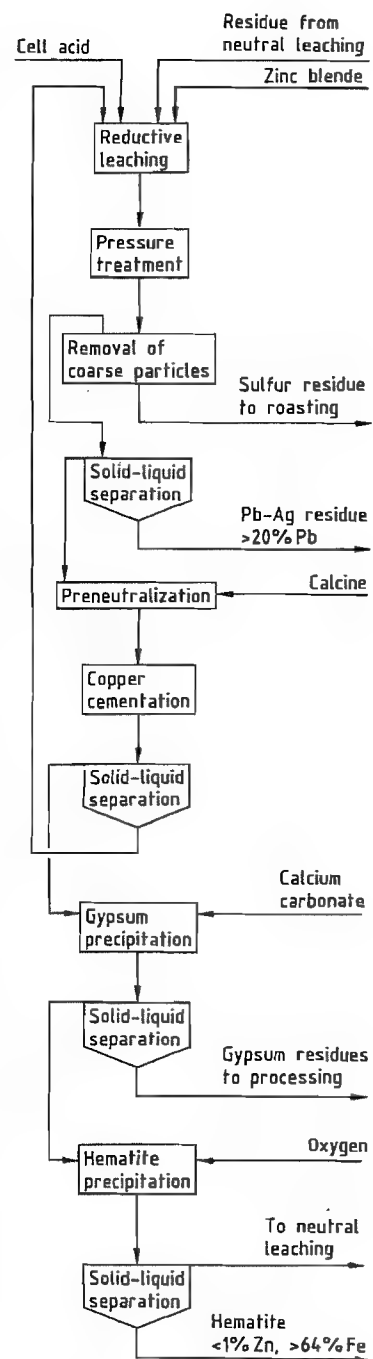


Figure 10.9: Flow diagram of the hematite process [3, p. 680].

10.5.5 Treatment of Leaching Residues

Residues from calcine leaching are primarily subjected to pyrometallurgical treatment. In some plants of older design, the residues from the neutral leaching stage are treated in a Waelz kiln. This removes the lead, and the resulting sinter oxide is ground and recycled to the leaching process. In a development of the classical Waelz kiln process, vaporization is carried out in a Waelz kiln fitted with an external burner. A rotary flame-fired furnace of the Dorschel type can also be used in a batch process.

A combination of flotation with pyrometallurgical and hydrometallurgical processes (sulfating roasting followed by leaching) enables the valuable metals to be recovered from the leaching residues.

10.5.6 Solution Purification

Impurities still present in the unpurified neutral liquors from the iron precipitation stage can lead to

- Lower current efficiency
- The presence of impurities in the cathodically deposited zinc
- Adverse effects on the anode and the cathode

If the critical impurity concentrations are exceeded and several impurities are present simultaneously, the electrolytic process may no longer be possible. The concentration limits of the harmful impurities cannot be precisely specified, but the following guidelines (in mg/L) can be used:

As	0.01–1
Sb	0.05–0.1
Ge	0.002–0.05
Ni	0.05–3.0
Co	0.1–1.0
Fe	20–30

In the formerly used iron hydroxide precipitation process, the adsorptive effect of the hydroxide precipitate caused most of the arsenic, antimony, and germanium to be removed along with the iron, so reducing their concentrations below the acceptable limits.

However, when the residues from the neutral leaching are subjected to hot acid leaching (mainly in the interest of higher zinc yields), the neutral liquors contain much higher levels of impurities. As these are not removed either in the iron precipitation or the leaching stage, careful purification of the liquor is necessary. In principle, there are the following possibilities:

- Chemical precipitation
- Electrochemical deposition
- Ion exchange (solvent extraction)
- Cementation with zinc

For high quality requirements, a combination of methods can be used. Chemical precipitation is mainly used for nickel and cobalt. For example, nickel can be precipitated by dimethylglyoxime and cobalt by α -nitroso- β -naphthol. However, as these reagents are expensive, their use can only be considered in exceptional cases for liquors with very low levels of impurities.

Processes involving the use of fluidized-bed electrolysis to remove impurities more noble than zinc and the use of solid and liquid ion exchangers are still at the development stage.

In most zinc electrolysis plants, the liquor is purified by cementation of harmful elements on zinc dust in a continuous, multistage process. An inert coating can form on the zinc particles or they may be chemically dissolved. Therefore, not all the zinc dust added can take part in the cementation process and a large excess of zinc dust (5–10 fold) is necessary to ensure effective purification.

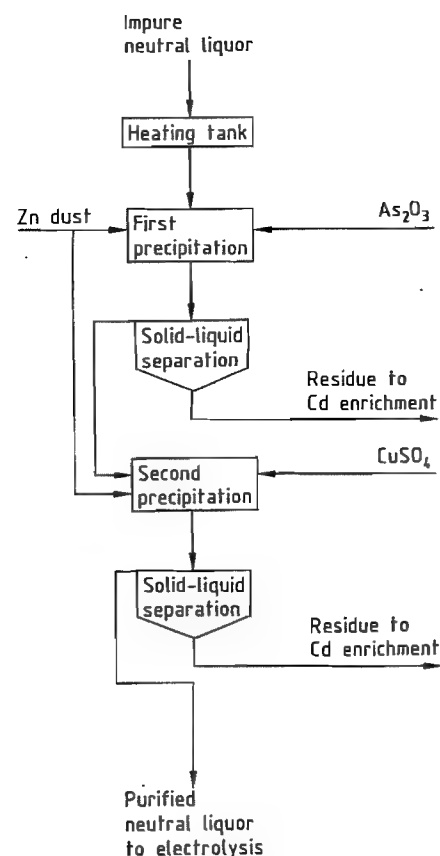


Figure 10.10: Hot-cold liquor purification [2, p. 607].

A typical process used in many plants is the hot-cold liquor purification process (Figure 10.10), which has two successive precipitation stages.

In the first stage, copper, nickel, and cobalt are precipitated by adding zinc dust in the presence of an added activator, usually As₂O₃. In the second stage, copper sulfate is the activator, and cadmium is removed. In many cases, a third fine purification stage is included.

The conventional hot-cold liquor purification process has a number of disadvantages:

- The necessity of adding copper if too little copper is present in the starting materials
- The possibility of releasing highly toxic arsine

- The presence of the impurities arsenic and antimony in the precipitated copper
- The possibility that the precipitated metals may redissolve

These disadvantages have led to the development of the alternative reversed liquor purification process (Figure 10.11). Here, it is not necessary to add copper to remove cobalt and other impurities. The low concentrations of arsenic are sufficient to act as activator, the costly copper additions are avoided, and relatively pure cementates are obtained in both precipitation stages. This process can also be operated continuously, whereby the addition of zinc dust is controlled by measuring the electrode potential, which is a function of the copper and cadmium concentrations in the liquor.

10.5.7 Electrolytic Production of Zinc [1–5, 10, 13]

Principles of Zinc Electrolysis. As the standard electrode potential of Zn²⁺ is -0.763 v, a solution of zinc sulfate should not deposit zinc on electrolysis: hydrogen should be liberated instead. Zinc deposition is only possible because of the hydrogen overvoltage at the zinc electrode, which causes a voltage shift of magnitude approximately equivalent to the standard electrode potential of zinc. The overvoltage is influenced by a number of factors. For example, the effect of current density is expressed by the Tafel equation:

$$\eta = a + b \log i$$

It decreases with increasing temperature, but, as the conductivity decreases with decreasing temperature, the energy consumption increases. With these effects in mind, two typical methods of performing zinc electrolysis were used in industry for a long time. Either the electrolytes were slightly acidic and current densities were ca. 325 A/m² or they were strongly acidic and current densities were ca. 850 A/m². The process parameters widely used today give good current yields in zinc electrolysis using current densities in the

range 400–600 A/m² and a process temperature not exceeding 40 °C.

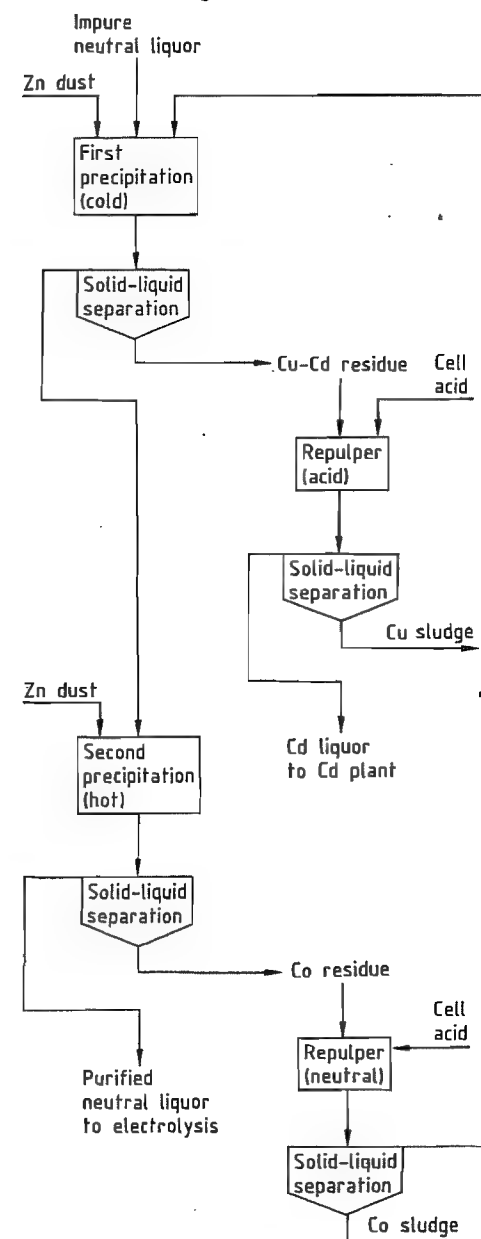


Figure 10.11: Reversed liquor purification [2, p. 608].

However, the hydrogen overvoltage is also influenced by the condition of the surface of the electrodes. Smooth surfaces lead to high

overvoltages. For this reason, the cathode plate must be stripped every other day in practical operation. Zinc electrolysis is extremely sensitive to impurities in the electrolyte. These fall into several groups:

- Impurities that are more electronegative than zinc, e.g., potassium, sodium, calcium, magnesium, aluminum, and manganese. These impurities do not directly interfere with the electrolytic process. If concentrations are too high, the viscosity of the electrolyte increases and the diffusion processes in the boundary layers are disturbed. A limit of 60 g/L is used as a guideline figure.
- Impurities whose electrode potential lies between those of Zn²⁺ and H⁺. In the case of lead, cadmium, thallium, and tin, the hydrogen overvoltage is higher than that of zinc. These metals are deposited and form impurities in the zinc. In the case of iron, cobalt, and nickel, the overvoltage is lower than of zinc. These are also deposited electrolytically but can be redissolved by the cell acid. Redox effects can lead to reduction in current yield. For this reason, the maximum tolerable concentrations are very low.
- Impurities that are more electropositive than zinc. These include copper, arsenic, antimony, indium, tellurium, and germanium. These lead to a reduction in the overvoltage. The deposition of copper, nickel, cobalt, arsenic, and antimony can have a strongly detrimental effect on current yield due to the formation of local elements on the cathode, leading to dissolution of the zinc. For this reason, the maximum tolerable concentrations of these impurities are also very low, and the zinc electrolytes must therefore be rigorously purified.

The Practice of Zinc Electrolysis. Zinc electrolysis is a complex system in which positive and negative factors, especially as they affect current yield, energy consumption, required purity of the liquor, and mechanization, must be balanced against each other.

The purification of the liquor is now so well controlled that lower current densities can be used, enabling the electrolysis time between

cathode changes to be extended from one to three days. Also, the cathode stripping operation, which involved heavy manual work, has been improved by the development of mechanical stripping equipment, and this has enabled cathodes with increased surface areas to be used.

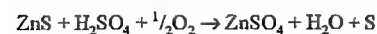
In general, the electrolytic cells are concrete baths cast in one piece and lined with polyethylene. Lead linings are no longer used in modern electrolysis plants. The cells are arranged in rows and connected in series. The electrolyte supply to each cell is usually individually controlled.

The cathode plates consist of sheet aluminum (99.5%), 5–7 mm thick, supported on carrier rods and provided with welded or plated copper contacts. The cathodes are polished at intervals of 4–6 weeks to prevent excessive adhesion of the cathode deposits. The latter problem can also be controlled by suspending the cathode plates in the bath and briefly running them as anodes.

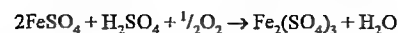
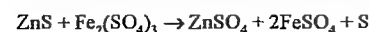
Anode materials are usually Pb–Ag alloys with a silver content of 0.25–0.75%. The anodes are usually made by casting the metal around a central copper carrier rod. Anodes that contain Sr and/or Ca and Ti in addition to Ag have higher strength and improved corrosion resistance.

10.5.8 New Developments in Zinc Production [2, 32]

Pressure Leaching of Sulfidic Zinc Concentrates. There have been many attempts to avoid the roasting process in the treatment of sulfidic zinc concentrates. For example, a process of pressure leaching of sulfidic concentrates has been developed by Sherritt Gordon Mines, Fort Saskatchewan, Alberta, Canada, and is used on an industrial scale. The process can be represented by the equation:



which consists of the partial reactions:



Dissolved iron originates either from marmatitic blende (Zn, Fe)S or pyrrhotite Fe_7S_8 , but not from pyrite, FeS_2 , which does not dissolve under these liquor conditions. This iron promotes the oxygen transfer reaction that converts the sulfide to sulfate.

The process is carried out in two stages, as shown schematically in Figure 10.12. The zinc concentrate is size reduced by wet grinding to $90\% < 44 \mu\text{m}$ and oxidatively leached in two stages at 150°C at an oxygen pressure of 1 bar. Exhausted electrolyte (cell acid) is used as solvent. In the first stage, 80% of the zinc present is dissolved, and in the second stage a further 18%.

The overflow from the thickener in the first stage, at a pH of 1.5–2.5, is treated with zinc oxide to neutralize the residual iron that was not precipitated in the autoclave, and the liquor so obtained is filtered and purified in the usual way. It is then fed to the zinc electrolysis stage.

The residue from the first stage is pumped together with cell acid into the autoclave of the second stage. After solid–liquid separation, the solution from the second stage is recycled to the first autoclave. The residue is washed in countercurrent flow to remove elemental sulfur if necessary, and the residual iron oxide is treated to recover lead and noble metals or disposed of, depending on its composition.

The process is used in two Canadian zinc smelting plants, one in Trail (Cominco), and the other in Timmins (Texas Gulf) in Ontario.

Direct Leaching of Oxidic Zinc Ores [2]. Some new methods of directly leaching oxidic ores (smithsonite, willemite, etc.) have been developed recently.

A willemite containing 40% zinc has been directly leached at the zinc smelting plant at Três Marias of the Companhia Mineira de Metais in Brazil. Smithsonite with a lower zinc content ($< 30\%$) is first enriched by treatment in a Waelz kiln, and the oxide obtained is then leached.

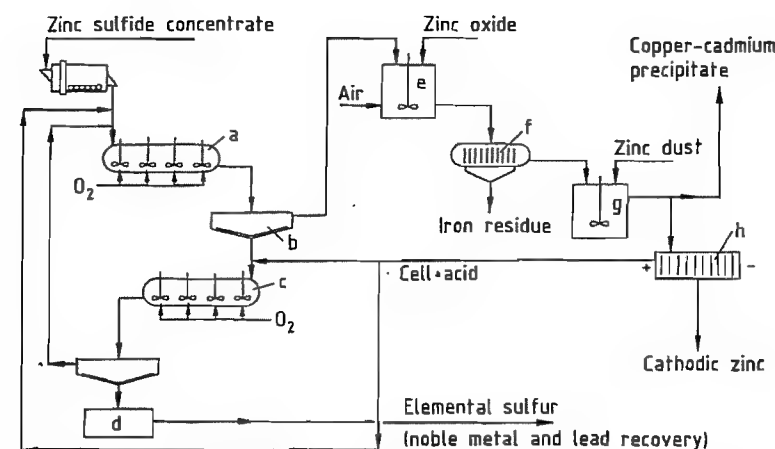


Figure 10.12: Pressure leaching of zinc concentrate [2, p. 610]: a) Pressure leaching, stage 1; b) Thickener; c) Pressure leaching, stage 2; d) Washing; e) Iron precipitation; f) Filtration; g) Cleaning tank; h) Electrolysis.

10.6 Uses and Economic Aspects

Two properties of zinc are of special relevance to its applications. Firstly, its standard electrode potential is considerably more positive than that of the construction material iron. Zinc coatings therefore provide very good corrosion protection for steel structures. Secondly, zinc has a relatively low melting point, which makes it suitable for use in pressure die casting of complex components.

10.6.1 Galvanizing [3, 33]

The ever-increasing need to make the best use of the world's raw material reserves means that corrosion prevention as a method of preserving the usefulness of commercial metals continues to increase in importance. Moreover, as the atmosphere becomes increasingly corrosive, standards of corrosion protection must continue to rise, especially in steel construction.

A zinc coating on steel ensures lasting protection against the corrosive effects of the weather by the following mechanisms:

- The effect on zinc of the carbon dioxide and moisture in the air is to form protective coat-

ings with a zinc carbonate basis, resulting in a low corrosion rate.

- Because of its electrochemical property of providing cathodic protection, zinc actively prevents the occurrence of corrosion in the region of small defects, damaged areas of coating, and cut edges of sheet.

In the industrialized countries, almost 50% of the zinc consumed is used for corrosion protection.

Commercial zinc (98.5–99.5%) is usually used for hot-dip galvanizing in production and jobbing plants, and high-purity zinc (99.95%) for the continuous galvanizing of steel strip or wire. The metallurgical processes used to produce the less pure grades of zinc mean that lead is the main impurity present. This is an advantage, as the presence of 1% lead reduces the surface tension of zinc by ca. 40% compared with that of the high-grade product. The components being galvanized are therefore more effectively wetted by the molten zinc.

During the process of immersion in the zinc bath, which takes only a few minutes, the component is heated to ca. 450°C . Diffusion processes cause layers of iron–zinc alloys to form on the steel surface, giving very good adhesion of the zinc coating.

Other galvanizing processes have been developed in addition to the hot-dip process. In

electrolytic galvanizing, a D.C. current causes the deposition of lustrous coating, 5–25 μm thick, from acidic, cyanide, or alkaline cyanide-free electrolytes. However, these only give protection against mildly corrosive media. In general, additional protection is provided by chromate passivation.

In the spray galvanizing process, zinc wire is melted in a fuel gas/oxygen flame or an electric arc at the jet of a spray pistol and is propelled by compressed air from a distance of 15 cm, giving a coating ca. 0.1 mm thick. The resulting purely mechanical adhesion of the zinc is inferior to that produced by alloy formation at the metal interface in hot-dip galvanizing.

10.6.2 Zinc as a Construction Material [2, 34]

Although zinc has fairly good strength properties, it was for a long time not used as a material of construction because of its very poor creep resistance. Low-alloy zinc grades based on Zn–Ti–Cu, which have very good ductility and creep resistance, were developed only ca. 40 years ago. This material can be rolled to form zinc plate or sheet which can be used in the manufacture of roof drainage components or for covering buildings. Recently, a wide range of shapes has been developed, enabling æsthetic appeal to be combined with protection of buildings from the rigors of nature.

10.6.3 Pressure Die Casting with Zinc [2, 35]

Pressure die casting is another major area of use and is dominated by alloys of the type ZnAl_4Cu_1 and modifications thereof. Some of the advantages of zinc for pressure die casting are:

- Production runs can be very large (60–1000 components), depending on the size and complexity of the components

- The dies are extremely durable, enabling up to 1×10^6 components to be produced from one die
- The low viscosities and low melting points of the alloys ensure a high definition product
- Dimensional accuracy is ensured as shrinkage of the zinc alloys is low and easily controlled
- Lustrous or matt surfaces can be obtained with various metallic coatings and effects
- Costs are low due to large production runs
- The products are durable because of their good mechanical and physical properties
- The energy requirements of manufacture are low

Approximately 50% of all zinc pressure die castings go to the automobile industry.

10.6.4 Zinc as a Chemical [2, 36]

Zinc-based chemicals, including zinc dust, account for ca. 12–15% of world's zinc consumption. Zinc oxide is quantitatively by far the most important zinc-based chemical product, followed by zinc dust, zinc sulfate, and zinc chloride in order of importance and quantity. All other zinc compounds are of minor importance.

World consumption figures for zinc oxide and zinc dust have remained constant for many years. However, the demand for zinc sulfate and chloride is decreasing. The rate of growth of the consumption of zinc thiocarbonate and zinc stearate matches that of rubber production, their main area of use. Zinc oxide, the compound most in demand, can be produced by various processes. Its purity and quality depend on the production method used. In the indirect (so-called French) process, pure zinc is heated and oxidized in a current of air. The very pure zinc oxide formed is collected as a powder in settling chambers where it separates into different particle sizes. This material is usually known as zinc white. In the direct (so-called American) process, the raw materials used are zinc ores or zinc by-products, which usually contain lead. A car-

bonaceous material is heated with the raw material, reducing it with formation of zinc vapor. This is oxidized with air and separated into particle size fractions.

The starting materials for wet chemical processes are solutions of purified zinc. Zinc carbonate or hydroxide is precipitated and is then filtered, washed, dried, and calcined at ca. 800 °C.

The various types of zinc oxide include an industrial grade, which is used as an intermediate product in the production of other chemicals; pigment grades, which include almost all the lead-containing grades; precipitated zinc oxides which have no pigment properties; and special grades such as the extremely finely-divided zinc oxide for photocopying paper.

The main consumer of zinc oxide is the rubber industry, in which it is used as a vulcanization activator and sometimes also as a filler.

Zinc oxide as a pigment in aqueous latex paints has lost a significant share of the market. Its use in agriculture as an additive to fertilizers to treat zinc deficiency in soils is of lesser importance. Zinc oxide is a component of formulations in the glass, enamel, and ceramic industries, where it influences the melting point and also the optical and elastic properties, color, and luster of the glaze. It is also a component of face powder, lipsticks, and creams used in the cosmetics industry. It is also used as an additive to lubricants, adhesives, drying agents, and delustering agents, and as a catalyst in methanol synthesis.

Zinc dust is produced by a similar process to that used for zinc oxide, but in a reducing atmosphere. There are two grades: pigment zinc dust and zinc dust for chemical use. Zinc dust is used as a pigment for anticorrosion paints and coatings whose primary function is to form an impermeable surface. The action of the environment leads to the formation of zinc carbonate and basic zinc compounds between the zinc particles, reinforcing this effect. These coatings also give cathodic protection, which is especially useful if there is slight damage to the coating layer.

10.6.5 Economic Aspects

The development of world zinc consumption in the important industrial countries and regions of the world is illustrated by the figures for the years 1980, 1985, and 1990, which are listed in Table 10.4.

10.7 Alloys

Zinc recrystallizes just above room temperature and has low creep resistance. It is therefore only suitable as a construction material when alloyed. The alloying elements, mainly Al, Cu, Ti, and Mg, cause grain refinement, mixed crystal formation, or precipitation hardening, thereby considerably improving the mechanical properties.

10.8 Compounds

10.8.1 Fluoride

Zinc fluoride, ZnF_2 , forms monoclinic tetragonal crystals with the rutile structure [37], m_p 872 °C [38], ρ_{25} 4.95 g/cm³. The solubility of $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ at 20 °C is only 1.62 g ZnF_2 in 1000 mL solution, but it is very soluble in aqueous ammonia. ZnF_2 reacts with sodium hydroxide solution to form flocculent precipitates of basic zinc fluorides.

Synthesis. $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ is formed when zinc carbonate or zinc oxide reacts with aqueous hydrofluoric acid. The water of crystallization can be driven off by heating to > 200 °C and/or in a vacuum.

Analysis. Calcined commercial zinc fluoride has the typical analysis 61–63% Zn, and 33–36% F, with the following maximum impurity levels: Fe 500 ppm, Pb 100 ppm, and SO_4 100 ppm.

Uses. Zinc fluoride is used as an additive to electrolytic galvanizing baths, in glazes and enamels for porcelain, and special types of glass with a high refractive index. It is also used as a flux for welding and soldering and as a fluorinating agent in organic syntheses.

Table 10.4: Development of zinc consumption.

	1981	1985	1990
Germany	405.7	408.8	484.0
Belgium	151.8	169.1	177.6
France	330.0	246.9	284.0
United Kingdom	181.3	189.3	189.0
Italy	236.0	218.0	278.0
Netherlands	45.2	51.1	71.7
Greece	18.8	15.2	20.3
Portugal	19.0	8.3	16.0
Spain	91.1	95.3	118.7
Finland	24.4	26.0	29.1
Yugoslavia	87.8	105.6	108.9
Norway	20.2	21.0	15.9
Austria	26.9	31.9	39.0
Sweden	38.0	31.5	39.5
Switzerland	25.2	26.3	22.3
Denmark	16.1	12.2	13.0
Other Europe	1.4	1.3	1.4
Europe	1719.1	1657.8	1908.4
Hong Kong	22.6	21.5	17.3
India	95.3	134.0	135.0
Indonesia	51.4	50.6	53.2
Japan	752.3	780.1	814.3
Malaysia	14.5	14.6	22.6
Pakistan	9.7	11.6	25.0
Philippines	16.1	13.0	33.1
Singapore	11.8	6.4	13.0
South Korea	68.0	119.7	227.4
Taiwan	38.4	49.4	79.4
Thailand	33.3	39.6	66.0
Turkey	12.3	49.8	47.7
Other Asia	13.3	38.2	52.8
Asia	1139.0	1328.5	1586.6
Egypt	2.7	7.0	10.0
Algeria	11.0	11.0	15.0
Ivory Coast	4.0	4.6	2.0
Kenya	7.2	6.7	8.2
Morocco	3.0	2.7	3.0
Nigeria	12.7	7.9	6.0
South Africa	84.1	84.1	86.5
Tanzania	3.2	3.5	2.0
Other Africa	8.6	9.3	18.3
Africa	136.5	136.8	150.0
Argentina	30.9	25.8	19.1
Brazil	155.9	132.4	129.7
Canada	140.0	156.5	126.1
Colombia	14.6	18.3	8.6
Mexico	88.9	99.2	110.1
Peru	23.2	41.2	71.0
Venezuela	20.2	15.4	10.6
United States	878.6	961.4	996.8
Other America	28.0	22.7	14.1
America	1380.3	1472.9	1486.5
Australia	95.4	82.1	82.2
New Zealand	20.7	24.7	20.0
Other Oceania	0.1	0.1	0.1
Oceania	116.2	106.9	102.3
Western countries	4491.1	4702.9	5234.7

	1981	1985	1990
Bulgaria	75.0	70.0	46.6
East Germany	86.2	69.7	45.5
Poland	178.3	157.2	109.5
Romania	49.9	35.3	12.8
Czechoslovakia	67.0	58.0	51.8
Soviet Union	1030.0	1000.0	920.0
Hungary	25.0	24.5	12.0
China	259.0	349.0	500.0
Others	28.0	32.0	45.0
Cuba	1.5	1.8	1.2
Eastern countries	1799.9	1797.5	1744.4
World total	6291.0	6500.4	6979.1

10.8.2 Chloride

Zinc chloride, ZnCl_2 , forms hexagonal-rhombic crystals, usually in the form of a white powder, mp 283 °C, bp 732 °C, ρ 2.91 g/cm³ at 25 °C, which is very soluble in water (432 g ZnCl_2 in 100 g water at 25 °C, 615 g ZnCl_2 in 100 g water at 100 °C). It is also soluble in alcohols, ether, acetone, ethyl acetate, glycerine, pyridine, amines, and nitriles.

Zinc chloride is strongly hygroscopic and forms hydrates with 1–4 mol water. It has a strong affinity for water, and causes many organic compounds to undergo condensation reactions. Considerable heat is evolved when ZnCl_2 dissolves in water.

Zinc chloride reacts with NH_4Cl to form the compounds $(\text{NH}_4)_2[\text{ZnCl}_4]$, $(\text{NH}_4)_3[\text{ZnCl}_5]$, and $(\text{NH}_4)_4[\text{ZnCl}_6]$. Analogous compounds are formed with amine hydrochlorides. Ammonia forms complexes with the composition $[\text{Zn}(\text{NH}_3)_x\text{Cl}_2]$ ($x = 2, 4, 6$). Amines give analogous compounds. In water, zinc chloride behaves as an acid, forming aquoacids with the compositions $\text{H}[\text{ZnCl}_2\text{OH}]$ and $\text{H}_2[\text{ZnCl}_2(\text{OH})_2]$. With increasing dilution, the aquoacid anions take up water and lose Cl^- , eventually being converted into the aquocation complex $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ and losing the strongly acid reaction.

Commercial zinc chloride often contains basic zinc salt which leads to cloudiness in aqueous media.

Production. High-purity zinc chloride is formed from zinc and HCl gas at 700 °C [39]. Spectroscopically pure zinc chloride can be

obtained by decomposing zinc amalgam with HCl [40]. Quality specifications are listed in Table 10.5.

Table 10.5: Quality specifications for zinc chloride.

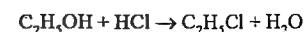
	Analytical-grade ZnCl_2 (ACS, ISO), %	High-purity ZnCl_2 (DAB, PhEur, BP, JP, USP), %
Assay (complexometric)	≥ 98	98–100.5
SO_4	≤ 0.002	< 0.01
Total N	≤ 0.001	< 0.01
As		< 0.0002
Ca	≤ 0.001	< 0.01
Fe	≤ 0.0005	< 0.001
K	≤ 0.001	0.001
NH_4	≤ 0.001	0.02
Na	≤ 0.001	
Oxychloride (as ZnO)	≤ 1.2	in accordance with test
pH (10% aq.)		4.6–5.5

Technical-grade zinc chloride is usually produced by leaching zinc oxides or zinc-containing waste such as zinc dross or ammonium chloride slags (unavoidable by-products of hot-dip galvanizing) with hydrochloric acid. Raw materials containing a high percentage of NH_3 must be subjected to an additional treatment stage, i.e., passing chlorine gas into the aqueous suspension to oxidize the ammonia to nitrogen.

The zinc-containing raw materials are dissolved in concentrated hydrochloric acid. The crude liquor contains varying amounts of the elements Fe, Mn, Pb, Cu, and Cd. Ferrous ion is oxidized to Fe^{3+} with H_2O_2 or KMnO_4 , and $\text{Fe}(\text{OH})_3$ is precipitated at pH 4.5. Also, the Mn is precipitated as MnO_2 by KMnO_4 . The remaining elements Cu, Pb, and Cd are removed by treatment with zinc dust (cementation). The solution is then evaporated to dryness. Aqueous solutions are sometimes subjected to further processing.

Uses

- Hydrochlorination of ethanol to monochloroethane



- Catalytic hydrolysis of benzotrichloride to benzoyl chloride

- Catalyst in the production of ammonium methylene-bis-dithiocarbamate from hydrogen peroxide, aqueous ammonia, carbon disulfide, and ethylenediamine

- Production of benzyl chloride from benzene, formaldehyde, and HCl/ZnCl_2
- Filling material for batteries, emulsion breaker in petrochemical processes, deodorizing agent
- Production of zinc compounds, e.g., zinc cyanide from potassium cyanide and a solution of zinc chloride (sometimes zinc sulfate)
- Production of zinc soaps from alkali metal soaps and zinc chloride

10.8.3 Bromide

Zinc bromide, ZnBr_2 , forms colorless rhombic crystals, mp 394 °C, bp 650 °C, ρ 4.29 g/cm³, which are strongly hygroscopic. The dihydrate, $\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}$, melts at 35–47 °C with loss of water of crystallization. It is obtained by dissolving an aqueous suspension of ZnO or metallic zinc in aqueous HBr . Anhydrous ZnBr_2 is formed from its elements at ca. 600 °C or by thermal dehydration of the dihydrate in a stream of dry CO_2 . Its solubility in water at 25 °C is 820 g/L.

Uses

- A mild Lewis acid for alkylation reactions [41]
- A catalyst for intramolecular reactions [42]
- An activating agent in the production of activated carbon
- An additive to photographic gelatins
- An electrolyte for zinc bromide batteries

High-purity ZnBr_2 contains $\geq 98\%$ ZnBr_2 , with the following maximum impurity contents: Ba 10 ppm, Ca 100 ppm, Fe 10 ppm, K 100 ppm, Mg 100 ppm, and Na 100 ppm.

10.8.4 Iodide

Zinc iodide, ZnI_2 , forms white to yellowish cubic crystals, mp 446 °C, bp 624 °C, ρ_{25} 4.73 g/cm³. It is produced by adding metallic zinc

to constant-boiling aqueous hydriodic acid until the yellow color disappears, by neutralizing aqueous HI with ZnO in the presence of a catalyst (precipitated silver), or by the reaction of I_2 vapor with molten zinc at 600 °C in a stream of N_2 [43]. Its solubility in water at 20 °C is 4500 g/L (hygroscopic).

Zinc iodide is used in medicine as a topical antiseptic astringent and in the preparation of iodide–zinc–starch solution.

10.8.5 Sulfate

Zinc sulfate, $ZnSO_4$, ρ 4.33 g/cm³, forms rhombic crystals. On heating to > 650 °C, zinc sulfate undergoes considerable decomposition with formation of basic sulfates. Above 800 °C, it decomposes completely into ZnO and SO_3 .

$ZnSO_4$ is very soluble in water, and forms hydrates with 1, 2, 4, 6, and 7 molecules of water of crystallization. The hepta-, hexa-, and monohydrates are produced on an industrial scale.

Zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$, forms white, lustrous, columnar, rhombic crystals. It is transformed into the hexahydrate at 39 °C. It occurs in nature as goslarite. Mixed crystals are formed with the sulfates of Fe, Mg, Mn, Co, and Ni. It is very soluble in glycerine, but only sparingly soluble in other organic solvents.

Zinc sulfate is obtained by leaching zinc-containing materials with sulfuric acid in an aqueous medium. Suitable materials include zinc dross, slags, sweepings, oxides, sludges, metallic zinc, and zinc-containing flue dusts [44]. Used sulfuric acid can be utilized. It should be noted that arsine can be formed during the treatment of metallic dross and waste. Iron, manganese, and heavy metals are removed by the same process as that used to treat electrolyte liquors.

The purified solution of zinc sulfate is evaporated until its density reaches ca. 1.4 at 80 °C. On cooling, crystals of zinc sulfate heptahydrate form and are centrifuged off.

The crystals obtained are sometimes dried at ca. 30 °C to prevent efflorescence.

Pharmaceutical-grade $ZnSO_4 \cdot 7H_2O$ can be produced from sulfuric acid and pharmaceutical-grade zinc oxide. The impurity levels in the various grades of zinc sulfate are listed in Table 10.6.

Table 10.6: Commercial grades of $ZnSO_4 \cdot 7H_2O$.

	Analytical-grade	High-purity (DAB, USP, PhEur, FCC)	Pure
Assay	≤ 99.5%	99.5%	98%
As	0.5 ppm	2 ppm	10 ppm
Ca	10 ppm	50 ppm	
Cd	2 ppm	2 ppm	30 ppm
Cu	5 ppm	1 ppm	10 ppm
Fe	5 ppm	10 ppm	30 ppm
K	10 ppm	100 ppm	
Mg	10 ppm	50 ppm	
Mn	2 ppm	10 ppm	50 ppm
Na	50 ppm	1000 ppm	
Pb	5 ppm	5 ppm	50 ppm
Chloride	5 ppm	100 ppm	4000 ppm
Hg		1 ppm	
Se		5 ppm	
pH (5%, 20 °C)	4.4–5.6	4.4–5.6	

Zinc sulfate monohydrate, $ZnSO_4 \cdot H_2O$, is produced by thermal dehydration or by dehydrating with 95% ethanol. It crystallizes from a zinc sulfate mother liquor at temperatures above 70 °C [45]. It can be dried in a rotary, spray, or fluidized-bed driers.

Uses of zinc sulfate can be divided into direct and indirect uses.

Direct uses:

- Precipitating baths for viscose manufacture
- Electrolytes for galvanizing baths
- Additive (trace element) in fertilizers and animal feeds
- In medicine, as an emetic, astringent, or disinfectant
- Wood preservative, additive for paper bleaching, flocculent
- Water treatment

Indirect uses:

- Starting material for the production of other zinc compounds such as the fungicides Zineb and Mancozeb, zinc soaps, and the antidandruff agent zinc pyrithione

- Production of lithopone and zinc sulfide pigments
- Production of zinc cyanamide from potassium cyanamide
- Production of zinc phosphides

10.8.6 Toxicology and Occupational Health

Zinc metal and most of its compounds show very low toxicity compared to most other heavy metals. The toxicity of zinc salts varies to a certain extent, being dependent primarily on the toxicity of the anionic part of the compound. For example, the high toxicity and carcinogenicity of zinc chromate, $ZnCrO_4$, is not due to Zn^{2+} , but to the anionic CrO_4^{2-} component.

Intoxications with zinc and its compounds are comparatively rare. They can occur by ingestion of food contaminated with zinc leached from food containers or by inhalation of zinc or zinc oxide dust under occupational conditions (see below).

On the other hand, zinc is one of the most important essential elements for humans and all forms of plant and animal life. It is necessary for growth, skin integrity and function, testicular maturation, immunocompetence, wound healing, and for a variety of metabolic processes including carbohydrate, lipid, protein and nucleic acid synthesis or degradation. It is an essential, coenzyme-like component for the function of more than 70 metallo-enzymes, including alcohol dehydrogenase, carbonic anhydrase, and carboxypeptidase [46]. Physiological amounts of zinc have been shown to decrease the toxicity of other heavy metal ions such as Cd, Hg, Pb, and Sn [47].

Biological significance, biochemistry, toxicokinetics, human and animal toxicity, levels of tolerance, detoxification, evaluation of health risks to humans, and ecotoxicity of zinc and its compounds have been reviewed [47–50].

Toxicokinetics. As an essential element, zinc is absorbed in an active transport process, regulated by dietary zinc status and occurring pri-

marily in the ileum [51]. Zinc is bound to proteins to a large extent. Excretion occurs predominantly via the feces, and to a minor extent via urine and sweat. Excretion in the urine is up to 12.2 mmol/d; higher values indicate zinc intoxication [52].

Zinc is the most prevalent metal ion in human tissues other than blood. The body of a 70-kg man contains ca. 2.3 g of zinc [53], 64% of which is found in muscle and 28% in bone [54]. The highest zinc concentrations are found in reproductive organs, especially the prostate gland (87 µg/g wet weight), whereas the whole-body average is 33 µg/g wet weight [53]. Serum contains 10.7–22.9 mmol/L, plasma 17.4 ± 1.8 mmol/L, erythrocytes 184–198 mmol/L, and hair 3.30 ± 1.33 mmol/g [52].

Acute Toxicity. In contrast to numerous other heavy metals, zinc shows low acute toxicity. Zinc overload of the organism is rather unlikely and occurs almost exclusively by ingestion when food or drinks, especially acidic ones, are prepared or stored in galvanized containers [55, 56].

Symptoms of acute intoxication are gastrointestinal distress, diarrhea, nausea, and abdominal pain. Vomiting occurs almost universally. In elemental-zinc overdose, symptoms such as lethargy, slight ataxia, and difficulty in writing also appear. Abnormal laboratory parameters include increase of pancreatic enzyme activities, hypokalemia secondary to acute pancreatitis, and microhematuria [57, 58].

Zinc chloride, $ZnCl_2$, is caustic to the gastrointestinal tract, occasionally leading to hematemesis, beside the symptoms mentioned above. Furthermore, it is extremely detrimental to the lungs. An episode of pulmonary exposure to $ZnCl_2$ smoke resulted in ten fatalities due to pulmonary toxicity. Most survivors showed lachrymation, rhinitis, dyspnea, stridor, and retrosternal chest pain. In two autopsies, severe inflammation of the upper respiratory tract mucosa and pulmonary edema, but no changes in liver and kidneys, could be detected [59].

Zinc or zinc oxide fume is responsible for a syndrome which may occur in welding, galvanizing, or smelting operations, called "metal fume fever". Symptoms such as rapid breathing, dyspnea, cough, fever, shivering, sweating, chest and leg pain, myalgias, fatigue, metallic taste, salivation, thirst, and leukocytosis appear within 4–6 h after exposure and disappear after 24–48 h [60, 61]. The X ray of the chest is normally clear. A rapid tolerance (tachyphylaxis, "quick immunity" [62]) develops in workers within 48 h, but may be lost over the weekend ("monday morning fever"). Metal fume fever can also be caused by exposure to fumes of aluminum, antimony, copper, iron, magnesium, manganese, and nickel.

Zinc phosphide, Zn_3P_2 , is extremely toxic because of the formation of phosphine, PH_3 , on reaction with water or acids.

Chronic Toxicity. The development of a toxicosis has been reported in the case of a continuous uptake of drinking water contaminated with 40 ppm Zn from a galvanized pipe [63]. Dialysis patients are at risk of an elevation of the plasma concentration of zinc (and other heavy metal ions) [64, 65]. The symptoms are similar to those of acute toxicity, but are less pronounced.

Genotoxicity. Zinc apparently does not show any mutagenicity or carcinogenicity [47]. In human lymphocytes, 0.1–1000 $\mu\text{mol/L}$ of zinc acetate, alone or in combination with cadmium and lead acetates, failed to induce chromatid-type aberrations (deletions, acentric fragments) and gaps [66]. The carcinogenic effect of zinc chromate, ZnCrO_4 , is due to the chromate anion, not to the zinc cation.

Reproductive Toxicity. There are no indications for reproductive effects, especially for teratogenicity, of zinc [47].

Immunotoxicity. There are no reports concerning immunotoxic effects of zinc. However, zinc chromate, ZnCrO_4 , shows strong sensitizing effects and therefore is able to cause obstinate eczema under occupational conditions [67].

Toxicological Data. The lethal dose of ZnCl_2 in humans is 35 g. Since zinc sulfate, ZnSO_4 , is less caustic than the chloride, it has lower toxicity [68].

Treatment. Decontamination of the gastrointestinal tract after oral uptake of zinc compounds by syrup of ipecac, lavage, or cathartics is mostly unnecessary, since patients usually vomit sufficiently. For normalization of zinc levels, CaNa_2EDTA is the agent of choice [57, 59]. After oral uptake of ZnCl_2 , milk may be administered to decrease absorption of the metal [70].

After contact of the skin with ZnCl_2 , immediate removal is necessary using soap and plenty of water.

After contact of the eyes with ZnCl_2 , adequate measures are rinsing with plenty of water, use of Isogutt eye drops, and contacting an ophthalmologist as soon as possible [70, 71].

In cases of ZnCl_2 fume inhalation, cortisone preparations should be applied immediately (e.g., by inhalation of Auxiloson) to avoid development of lung edema [71]. In severe cases clinical observation for at least 24 h is necessary.

Occupational Health. The MAK value of zinc oxide, ZnO , is 5 mg ZnO/m^3 , measured as total fine dust [72]. The same TLV value has been set in Hungary, Japan, Poland, Sweden, and by the WHO, while it is 10 mg ZnO/m^3 in Bulgaria, Romania, and Pennsylvania (United States); it is 15 mg ZnO/m^3 in Finland. The United States has a TLV value of 1 $\text{mg ZnCl}_2/\text{m}^3$, and Massachusetts a 30-min limit of 0.2 mg/m^3 zinc chromate, ZnCrO_4 [53].

Zinc chromate, ZnCrO_4 is classified in group A1 (proven human carcinogens) of Appendix III of the MAK list [72].

10.9 Zinc Pigments

10.9.1 Zinc Sulfide Pigments [73–75]

White pigments based on zinc sulfide were first developed and patented in 1850 in

France. Although they are still of economic importance, they have continually lost market volume since the early 1950s when titanium dioxide was introduced. Only one modern production installation for zinc sulfide pigments still exists in the market-economy-oriented industrial nations (Sachtleben Chemie, Germany). There are other production plants in eastern Europe and in China.

The zinc-sulfide-containing white pigment with the largest sales volume is *lithopone*, which is produced by coprecipitation and subsequent calcination of a mixture of zinc sulfide, ZnS , and barium sulfate, BaSO_4 . Pure zinc sulfide is marketed as *Sachtolith*.

White zinc sulfide pigments maintain their market position in areas of use where not only their good light scattering ability but other properties such as low abrasion, low oil number, and low Mohs hardness are required. They are often produced from many types of industrial waste. This recycling relieves pressure on the environment, as these materials would otherwise have to be disposed of.

10.9.1.1 Properties

Some physical and chemical properties of ZnS and BaSO_4 are given in Table 10.7.

A white pigment must not absorb light in the visible region (wavelength 400–800 nm), but should disperse incident radiation in this region as completely as possible. The spectral reflectance curves of zinc sulfide and barium sulfate (Figure 10.13) fulfil these conditions to a large extent. The absorption maximum for ZnS at ca. 700 nm is a result of lattice stabilization with cobalt ions, whose function is explained in the next section. The absorption edge in the UV-A region is responsible for the bluish-white tinge of zinc sulfide. Depending on the production process, zinc sulfide has a sphalerite or wurtzite lattice type.

Table 10.7: Properties of the components of zinc sulfide pigments.

Property	Zinc sulfide	Barium sulfate ^a
<i>Physical properties</i>		
Refractive index n	2.37	1.64
Density, g/cm^3	4.08	4.48
Mohs hardness	3	3.5
Solubility in water (18 °C), %	1.8×10^{-4}	2.5×10^{-4}
<i>Chemical properties</i>		
Resistance to acids/bases	soluble in strong acids	insoluble
Resistance to organic solvents	insoluble	insoluble

^a Component of lithopone.

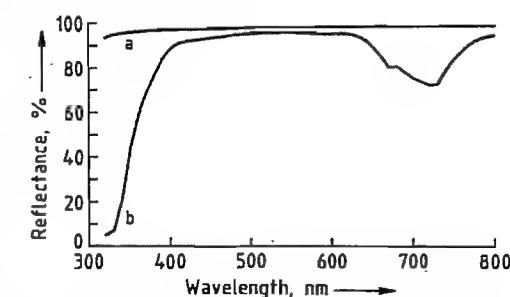


Figure 10.13: Spectral reflectance curves of barium sulfate and zinc sulfide: a) Barium sulfate; b) Zinc sulfide (Co-doped).

The refractive index n of ZnS , which determines its scattering properties, is 2.37 and is much greater than that of plastics and binders ($n = 1.5$ –1.6). Spheroidal ZnS particles have their maximum scattering power at a diameter of 294 nm. Barium sulfate does not directly contribute to the light scattering due to its relatively low refractive index ($n = 1.64$), but acts as an extender, and increases the scattering efficiency of the ZnS .

The barium sulfate in lithopone can be identified thermoanalytically by a reversible endothermic transformation at 1150 °C. Both Sachtolith and lithopone are thermally stable up to ca. 550 °C in the presence of air. Due to their low Mohs hardness, they are less abrasive than other white pigments. Barium sulfate is practically inert toward acids, bases, and organic solvents. Zinc sulfide is stable in aqueous media between pH 4 and 10, and is largely inert toward organic media. In the presence of

water and oxygen, it can be oxidatively decomposed by the action of UV radiation.

10.9.1.2 Production

Raw Materials. The source of zinc can be zinc oxide from a smelter, zinc dross or sweepings, ammonium chloride slag from hot dip galvanizing, or liquid waste such as pickle liquors from galvanizing plants. Variations in the price of zinc have a large effect on the economics of zinc sulfide pigments.

The starting material for water-soluble barium compounds is fused barium sulfide produced by coke reduction of naturally occurring barite with a low silica and strontium content. Suitable barite is readily available from many deposits worldwide.

Lithopone. The reaction of equimolar quantities of ZnSO_4 and BaS produces a white, water-insoluble coprecipitate with the theoretical composition 29.4% ZnS and 70.6% BaSO_4 :



By using a different molar ratio, this composition can be changed; for example, precipitation according to Equation (2) gives a product containing 62.5% ZnS and 37.5% BaSO_4 :



Figure 10.14 is a flow diagram of lithopone production. The solutions of zinc salts contain impurities (e.g., salts of iron, nickel, chromium, manganese, silver, cadmium) that depend on their origins. The main sources of zinc sulfate solutions are zinc electrolyses and the reprocessing of zinc scrap and zinc oxide. The first stage of purification consists of chlorination. Iron and manganese are precipitated as oxide-hydroxides, and cobalt, nickel, and cadmium as hydroxides. The solutions are then mixed with zinc dust at 80 °C. All the elements more noble than zinc (cadmium, indium, thallium, nickel, cobalt, lead, iron, copper, and silver) are almost completely precipitated, while zinc goes into solution. The metal slime is filtered off and taken to copper smelters for recovery of the noble metal components. A small quantity of a water-soluble

cobalt salt is added to the purified zinc salt solution. The cobalt (0.02–0.5%) becomes incorporated into the ZnS lattice during subsequent calcination to stabilize the final product against light. Zinc sulfide that is not treated in this way becomes gray in sunlight.

The *barium sulfide solution* is produced by dissolving fused barium sulfide in water. The barium sulfide is obtained by reducing an intimate mixture of crushed barite (ca. 1 cm lumps) with petroleum coke according to Equation (3) in a directly heated rotary kiln at 1200–1300 °C:

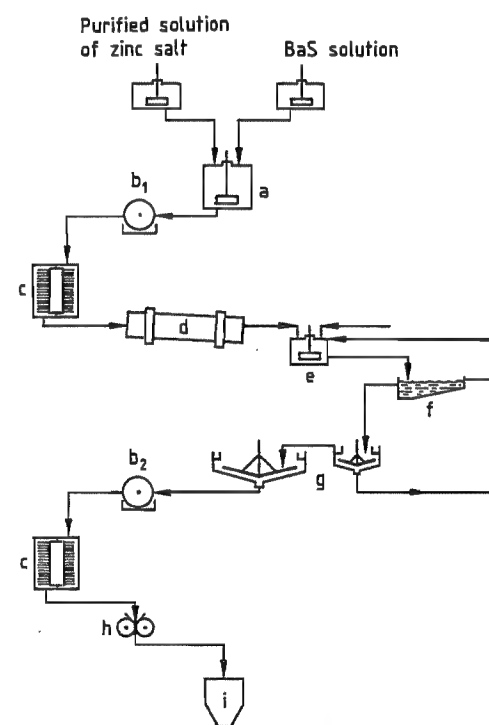


Figure 10.14: Flow diagram for lithopone production: a) Precipitation vessel; b) Rotary filter; c) Turbo dryer; d) Rotary kiln; e) Chilling vessel; f) Rake classifier; g) Thickener; h) Grinder; i) Silo.

The warm solution (60 °C) containing ca. 200 g/L barium sulfide is filtered and immediately pumped to the precipitation stage. Further purification is not necessary. Unreacted gangue and heavy metals are collected as insoluble sulfides in the filter cake. The almost clear so-

lution can be stored only for a short period. Longer storage leads to undesirable polysulfide formation.

The zinc salt and BaS solutions are mixed thoroughly under controlled conditions (vessel geometry, temperature, pH, salt concentration, and stirring speed, see (a) in Figure 10.14). The precipitated "raw lithopone" does not possess pigment properties. It is filtered off (b₁) and dried (c); ca. 2 cm lumps of the material are calcined in a rotary kiln (d) directly heated with natural gas at 650–700 °C. Crystal growth is controlled by adding 1–2% NaCl , 2% Na_2SO_4 and traces of Mg^{2+} (ca. 2000 ppm) and K^+ (ca. 100–200 ppm). The temperature profile and residence time in the kiln are controlled to obtain ZnS with an optimum particle size of ca. 300 nm.

The hot product from the kiln is quenched in water (e), passed via classifiers and hydroseparators (f) into thickeners (g), filtered on rotary filters (b₂), and washed until salt-free. The dried product is ground in high-intensity mills (g) and may undergo organic treatment (with a polyalcohol) depending on the application.

Figure 10.15 shows a scanning electron micrograph of lithopone. The ZnS and BaSO_4 particles can be distinguished by means of their size. The average particle diameter of BaSO_4 is 1 μm.

Sachtolith. Production is similar to that of lithopone. For process engineering reasons, a sodium sulfide solution is used as the sulfide component, and is formed according to Equation (4):



The BaSO_4 , which is produced as a by-product, is filtered, washed, dried, and ground. It is a high-quality extender (Blanc fixe) used in the paint industry.

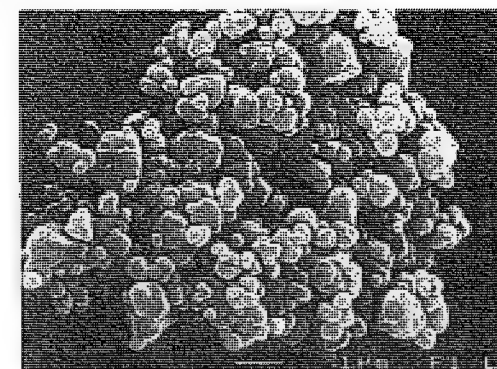


Figure 10.15: Scanning electron micrograph of lithopone. The larger particles are barium sulfate (mean size 1.0 μm) and the smaller particles are zinc sulfide (mean size 0.3 μm).

The Na_2S solution is mixed with a cobalt-treated zinc salt solution under precisely controlled conditions. The resulting zinc sulfide precipitate is calcined and processed to give the finished product.

Hydrothermal Process. Crystal growth of ZnS can be achieved by a hydrothermal process instead of by calcination. The raw lithopone is precipitated with a slight excess of sulfide at pH 8.5. The pH is then adjusted to 12–13 with sodium hydroxide solution, and 0.5% sodium carbonate is added. The suspension is then autoclaved for ca. 15–20 min at 250–300 °C. In contrast to the wurtzite structure of the calcined product, the hydrothermal product has a sphalerite structure with a ca. 10% greater scattering power. Although the product is of better quality, the hydrothermal process is less economic due to the high cost of the materials required for lining the autoclave (e.g., tantalum or a zirconium alloy).

Environmental Protection. During the reduction of barite and the calcination of Sachtolith and lithopone, sulfur dioxide is liberated. This is removed from the waste gas in a purification stage which is based on the reversible, temperature-dependent solubility of sulfur dioxide in polyglycol. The absorbed sulfur dioxide can be recovered as a liquid product or as a raw material for sulfuric acid. Any soluble barium in the residue from the dissolution of the fused BaS is removed by

treatment with iron-containing waste hydrochloric acid. The gangue, in the form of a slime, is water-insoluble and can therefore be disposed of. The barium chloride solution is used as a raw material for the production of precipitated barium sulfate fillers.

10.9.1.3 Commercial Products

Commercial lithopone grades contain 30% ZnS (red seal) and 60% ZnS (silver seal). The ZnS content of Sachtolith is > 97%. Various chemical (e.g., polyalcohols, siloxanes, silanes) and mechanical treatments (e.g., jet milling) are used to obtain other products for special applications. The technical data for commercial red seal lithopone and Sachtolith are given in Table 10.8.

Table 10.8: Technical data for red seal lithopone and Sachtolith.

Parameter	Standard	Sachtolith	Red seal lithopone
ZnS, %	DIN 55910	≥ 97	ca. 29
ZnO, %	DIN 55910	0.2	0.1
BaSO ₄ , %	DIN 55910	≤ 3	ca. 70
Brightness ^a		98	98–99
Lightening power	DIN 53192	400	120
Water-soluble salts, %	DIN 53197	< 0.2	< 0.2
Sieve residue ^b , %		0.02	< 0.1
Oil number	DIN 53192	12	8
pH	DIN 53200	6–8	7
Specific surface area, m ² /g		8	3

^aBaSO₄ white standard = 100.

^bTest sieve 45 μm, DIN 4188, ISO DIS 3310/1.

10.9.1.4 Uses

Lithopone is mainly used in coating materials with relatively high pigment concentrations (Table 10.9). Examples are primers, plastic masses, putties and fillers, artists' colors, and emulsion paints. An important property of lithopone is its low binder requirement, giving paint products with good flow and application properties. It is suitable for almost all binder media, and has good wetting and dispersing properties. With optimum feed composition, good dispersion can be achieved

simply by the action of a dissolver. It can be economically advantageous to use lithopone in combination with TiO₂ pigments; the good hiding power of the TiO₂ pigments is combined with the economic and technical advantages of lithopone. Due to the strong shift of the absorption band towards the blue, lithopone is especially useful as a white pigment for UV-cured paint systems. Zinc compounds have a fungicidal and algicidal action, and inclusion of lithopone or Sachtolith in paint formulations for exterior use therefore prevents attack by algae or fungi.

Table 10.9: Uses of Sachtolith and lithopone (as percentage of total consumption).

Use	Sachtolith	Lithopone	
		Western Europe	World
Paints	20	79	94
Plastics	64	17	2
Lubricants	6		
Others	10	4	4

The material advantages of lithopone are used in plastics (e.g., good lightfastness and clear bluish-white shade). The product also imparts very good extruding properties to the plastic resulting in high throughput rates and economic extruder operation. In fire-resistant systems, ca. 50% of the flame retardant antimony trioxide can be replaced by nontoxic lithopone without any adverse effect.

Sachtolith is mainly used in plastics (Table 10.9). Functional properties such as lightening and hiding power are criteria for the use of Sachtolith. It has proved to be very useful for coloring many thermoplasts. During the dispersion process it does not cause abrasion of metallic production machinery or adversely effect the polymer, even at high operating temperatures or during multistage processing. Even ultrahigh molecular mass thermoplasts can be colored without problems. In glass-fiber-reinforced plastics, the soft texture of Sachtolith prevents mechanical fiber damage during extrusion. Sachtolith is also used as a dry lubricant during the fabrication of these materials.

The low abrasiveness of Sachtolith prolongs the operating life of stamping tools used in the manufacture of industrial rubber articles. The lightfastness and ageing resistance of many elastomers are improved by Sachtolith. It is also used as a dry lubricant for roller and plain bearings, and as a white pigment for greases and oils.

10.9.1.5 Economic Aspects

Total world production of lithopone in 1990 was 220×10^3 t. This was subdivided as follows (10^3 t):

Germany	30 (+ 7 Sachtolith)
Former Yugoslavia	5
Former Czechoslovakia	15
Former Soviet Union	50
China	120

Only estimated figures are available for the former Soviet Union and China.

A decrease in output is to be expected because replacement by TiO₂ is not yet at an end, especially in coating materials. In the long term, only the high-quality grades can maintain their place in the market, i.e., those in which technical properties are required in addition to light scattering.

10.9.1.6 Toxicology

The use of zinc sulfide and barium sulfate in contact with foods is permitted by the FDA (United States) and in most European countries. Some restrictions apply in France, Italy, the United Kingdom, and Czechoslovakia.

Soluble zinc is toxic in large amounts, but the human body requires small quantities (10–15 mg/d) for metabolism. Zinc sulfide is completely harmless in the human due to its low solubility. The acid concentration in the stomach and the rate of dissolution following ingestion are not sufficient to produce physiologically significant quantities of soluble zinc. LD₅₀ values in the rat exceed 20 g/kg. No cases of poisoning or chronic damage to health have been observed in the manufacture of zinc sulfide pigments despite exposure to dust that occurs mainly during grinding and packing.

10.9.2 Zinc Oxide (Zinc White)

[76–80]

10.9.2.1 Introduction

Zinc oxide, ZnO, was formerly used only as a white pigment, and was named zinc white (C.I. Pigment White 4), Chinese white, or flowers of zinc. The term zinc white now denotes zinc oxide produced by the combustion of zinc metal according to the indirect or French process.

Historical Aspects. Zinc oxide has long been known as a by-product of copper smelting. The Romans called it "cadmia" and used it as such in the production of brass. They also purified it for use in ointments by reduction followed by oxidation. In the Middle Ages, the alchemists thought that cadmia could be converted into gold.

In the mid-18th century, the German chemist CRAMER discovered that cadmia could be obtained by the combustion of metallic zinc. COURTOIS began to produce zinc white in 1781 in France, but it was not until 1840 that industrial production was started by LECLAIRE (indirect or French process). The use of this white pigment spread rapidly. Zinc oxide replaced white lead because it had the advantage of being nontoxic, of not darkening in the presence of sulfurous gases, and of having better hiding power.

Around 1850 S. WETHERILL of the New Jersey Zinc Company perfected a roasting furnace in which a grate was charged with coal and then covered with a mixture of zinc ore and coal. The zinc was reduced by the partial combustion of the coal and reoxidized at the furnace exit (direct or American process). These furnaces were subsequently improved but are now no longer used. During the second half of the nineteenth century, the use of ZnO in rubber was introduced to reduce the time needed for vulcanization. The discovery of the first organic accelerators for vulcanization in 1906 added to the importance of ZnO, which acts as an activator in these materials.

A third industrial production process exists but this wet process is less widely used.

10.9.2.2 Properties

Physical Properties. Zinc oxide is a fine white powder that turns yellow when heated above 300 °C. It absorbs UV light at wavelengths below 366 nm. Traces of monovalent or trivalent elements introduced into the crystal lattice impart semiconducting properties. The elementary particles of ZnO obtained by the thermal method may be granular or nodular (0.1–5 µm) or acicular (needle-shaped). Some physical properties are given below:

Density	5.65–5.68 g/cm ³
Refractive index	1.95–2.1
mp	1975 °C
Heat capacity	
25 °C	40.26 Jmol ⁻¹ K ⁻¹
100 °C	44.37 Jmol ⁻¹ K ⁻¹
1000 °C	54.95 Jmol ⁻¹ K ⁻¹
Thermal conductivity	25.2 Wm ⁻¹ K ⁻¹
Crystal structure	hexagonal, wurtzite
Mohs hardness	4–4.5

Chemical Properties. Zinc oxide is amphoteric; it reacts with organic and inorganic acids, and also dissolves in alkalis and ammonia solution to form zincates. It combines readily with acidic gases (e.g., CO₂, SO₂, and H₂S). It reacts at high temperatures with other oxides to form compounds such as zinc ferrites.

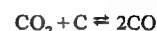
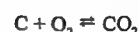
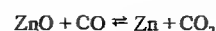
10.9.2.3 Production

About 1–2% of zinc oxide is produced by the wet process, 10–20% by the direct process, and the remainder by the indirect process.

Raw Materials. In the early days, the raw materials were mainly zinc ores or concentrates for the direct process, or metal from zinc producers for the indirect process. Nowadays, zinc oxide manufacturers mainly use residues and secondary zinc. This fact, combined with the demand for chemical purity imposed by the users, means that processes have had to be modified and a number of purification techniques are used.

Direct or American Process. The direct process is noted for its simplicity, low cost, and

excellent thermal efficiency. It consists of an initial high-temperature reduction (1000–1200 °C) of a zinc-containing material (as oxide), the reducing agent being coal. Reduction takes place according to Boudouard's equations:



The zinc vapor and the CO gas are then oxidized to zinc oxide and carbon dioxide above the reaction bed or at the furnace exit. Various zinc-containing materials are used, e.g., zinc concentrates, metallization residues, by-product zinc hydroxide, and above all zinc dross from casting furnaces or galvanizing. The dross must first be treated to remove chloride and lead by heating at ca. 1000 °C in rotary kilns.

Only rotary kilns are now used for the direct process; the use of static furnaces has been discontinued. The zinc content of raw materials is between 60 and 75%. There are two types of rotary kiln:

- One type is a long (ca. 30 m), fairly narrow (2.5 m diameter) kiln, heated by gas or oil. The raw material (a mixture of zinc-containing material and coal) is charged continuously either countercurrent or cocurrent to the combustion gases. The residues, which still contain some zinc and unburnt coal, leave the furnace continuously at the end opposite to the feed end. The excess coal is sieved out and recycled. The combustion gases, containing zinc vapor, ZnO, and CO, pass into a chamber where oxidation is completed and large particles of impurities settle out. The gases are then cooled in a heat exchanger or by dilution with air. The zinc oxide is collected in bag filters.
- The second type of rotary kiln is shorter (5 m) and has a larger diameter (ca. 3 m). Charging is continuous, but the dezincified residues are removed batchwise.

In both cases, operating conditions are controlled to obtain a high yield and to give the required particle shape and size. Provided no contamination is introduced, chemical purity is determined solely by the composition of the raw materials used.

Indirect or French Process. The zinc is boiled, and the resulting vapor is oxidized by combustion in air under defined conditions. The crystallographic and physical properties of the ZnO can be controlled by adjustment of the combustion conditions (e.g., flame turbulence and air excess). The chemical composition of the ZnO is solely a function of the composition of the zinc vapor.

Many types of furnace are available to produce vapor of the required purity from various raw materials and obtain a high yield of zinc. Pure zinc (super high grade, SHG; high grade, HG) or, to an increasing extent, metal residues (e.g., scrap zinc, die casting dross, or galvanizer's dross) are used as raw materials. Various liquid- or vapor-phase separation techniques are used for separating Cd, Pb, Fe, and Al from zinc metal before it is oxidized.

- **Muffle Furnaces or Retorts of Graphite or Silicon Carbide.** The metal is fed into the furnace either batchwise as a solid or continuously as a liquid. The heat of vaporization is supplied by heating the outside of the retort with a burner. The nonvolatile residues (iron and lead in the case of dross from smelting) accumulate in the retort and must be removed at intervals. This is facilitated by tipping the retorts.
- **Fractional Distillation.** The vapor containing Cd, Pb, Fe, Al, and Cu can be purified by fractional distillation in columns (New Jersey Zinc Co.) with silicon carbide plates. Oxidation takes place at the exit of the column.
- **Furnaces with Two Separate Chambers.** The metallic raw material, which can be in large pieces, is fed into the first chamber where it melts. This is connected to the second, electrically heated chamber where dis-

tillation takes place in the absence of air. The first version of this type of furnace was constructed by LUNDEVALL [81].

The nonmetallic residues are removed at the surface of the melting chamber. Impurities, such as Fe, Al, and some of the Pb, accumulate in the distillation chamber and are periodically removed in the liquid state. The last traces of lead are then removed by fractional distillation.

- **Smelting Process in a Rotary Kiln.** Indirect zinc oxide is also made by smelting in a rotary kiln, starting from the same raw materials. Melting, distillation, and part of the oxidation all take place in the same zone, allowing utilization of a large part of the heat of combustion of the zinc. By controlling the temperature and partial pressures of carbon dioxide and oxygen, the impurity content (Pb) can be limited and the shape and size of the ZnO particles can be adjusted, though to a lesser extent than in the other processes.

Wet Process. Zinc oxide is also produced industrially from purified solutions of zinc sulfate or chloride by precipitating the basic carbonate, which is then washed, filtered, and finally calcined. This method produces a grade of zinc oxide with a high specific surface area.

Products of this type are also obtained from waste hydroxides which are purified by a chemical route and then calcined.

Aftertreatment. Thermal treatment at temperatures up to 1000 °C improves the pigment properties of the ZnO and is mainly applied to oxide produced by the direct method. Controlled atmospheric calcination also improves the photoconducting properties of the high-purity oxide used in photocopying.

The ZnO surface is made more organophilic by coating it with oil and propionic acid. The ZnO is often deaerated and sometimes pelletized or granulated to improve handling properties.

10.9.2.4 Quality Specifications

Many standard specifications have been laid down for the more important uses of ZnO (rubber, paints, and the pharmaceutical industry). Various methods of classification are used, often based on the production process and the chemical composition. The most well-known are pharmacopeias, RAL 844 C3 (Reichs-Ausschuß für Lieferbedingungen), ASTM D79, BS 254, DAB 8 (Deutsches Arzneibuch), T 31006 NF (French standard), and ISO R 275. Table 10.10 shows the classification of commercially available zinc oxide grades.

Table 10.10: Classification of commercially available grades of zinc oxide.

Parameter	A	B	C	D
	Indirect process	Indirect process	Direct process	Wet process
ZnO (min.), %	99.5	99	98.5	93
Pb (max.), %	0.004	0.25	0.25	0.001
Cd (max.), %	0.001	0.05	0.03	0.001
Cu (max.), %	0.0005	0.003	0.005	0.00#
Mn (max.), %	0.0005	0.001	0.005	0.001
Water-soluble salts (max.), %	0.02	0.1	0.65	1
Loss on ignition (max.), %	0.3	0.3	0.3	4
Acidity, g H ₂ SO ₄ /100 g	0.01	0.1	0.3	0.2
Specific surface area, m ² /g	3–8	3–10	1–5	25 (min.)

Classification based on color codes is common in Europe, but is of limited value. Manufacturers have their own standards. In general, the terms silver seal and white seal indicate category A, and red seal category B.

10.9.2.5 Uses

Zinc oxide has many uses. By far the most important is in the *rubber industry*. Almost half the world's ZnO is used as an activator for vulcanization accelerators in natural and synthetic rubber. The reactivity of the ZnO is a function of its specific surface area, but is also influenced by the presence of impurities such as lead and sulfates. The ZnO also ensures good durability of the vulcanized rubber, and

increases its thermal conductivity. The ZnO content is usually 2–5%.

In *paints and coatings*, zinc oxide is no longer the principal white pigment, although its superb white color is used by artists. It is used as an additive in exterior paints for wood preservation. It is also utilized in antifouling and anticorrosion paints [82]. It improves film formation, durability, and resistance to mildew (having a synergistic effect with other fungicides) because it reacts with acidic products of oxidation and can absorb UV radiation.

The *pharmaceutical and cosmetic industries* use ZnO in powders and ointments because of its bactericidal properties. It is also used to form dental cements by its reaction with eugenol.

In the field of *glass, ceramics, and enamels*, ZnO is used for its ability to reduce thermal expansion, to lower the melting point, and to increase chemical resistance. It can also be used to modify gloss or to improve opacity.

Zinc oxide is used as a *raw material* for many products: stearates, phosphates, chromates, bromates, organic dithiophosphates, and ferrites (ZnO, MnO, Fe₂O₃). It is used as a source of zinc in animal feeds and in electro-galvanization. It is also used for desulfurizing gases.

Zinc oxide is used as a *catalyst* in organic syntheses (e.g., of methanol), often in conjunction with other oxides. It is present in some adhesive compositions.

The highest purity material is calcined with additives such as Bi₂O₃ and used in the manufacture of varistors [83]. The photoconducting properties of ZnO are used in photoreproduction processes. Doping with alumina causes a reduction in electrical resistance, hence, it can be used in the coatings on the master papers for offset reproduction [84].

10.9.2.6 Economic Aspects

The consumption of zinc oxide in Western Europe in 1990 was estimated to be 160 000 t. Annual world consumption is in the region of 500 000 t, representing ca. 10% of the total world zinc production. The rubber industry

consumes ca. 45% of the total and the remainder is divided among a large number of industries.

10.9.2.7 Toxicology and Occupational Health

Unlike other heavy metals, zinc is not considered to be toxic or dangerous. It is an essential element for humans, animals, and plants. The human body contains ca. 2 g, and it is recommended that 10–20 mg should be ingested per day [85]. The oral LD₅₀ value for rats is 630 mg/kg. The permitted concentration of the dust in air at the workplace is 5 mg/m³ (MAK), 10 mg/m³ (TLV-TWA). Values for zinc oxide fumes are 5 mg/m³ (TLV-TWA) and 10 mg/m³ (TLV-STEL).

If large quantities of ZnO are accidentally ingested or inhaled, fever, nausea, and irritation of the respiratory tract ensue after several hours. These symptoms rapidly disappear without long-term consequences.

10.9.2.8 Anticorrosive Zinc Oxide

Zinc oxide, ZnO, is a white powder that is usually used in combination with active anticorrosive pigments. It has the following physical properties:

Oil absorption value, g/100 g	20–24
Density, g/cm ³	5.6
Apparent density, cm ³ /100 g	100
Mean particle size, µm	0.11–0.22
BET surface area, m ² /g	3–10

The inhibiting action of zinc oxide is based on its ability to react with corrosive substances and to maintain an alkaline pH in the coating. It also reacts with acidic components of the binder to form soaps and absorbs UV light.

The lead content of commercial zinc oxide depends on the manufacturer and is in the range 0.002–1.5%. For a zinc oxide coating to be considered lead-free, the lead content must be less than 1.5%.

10.9.2.9 Transparent Zinc Oxide

Similar to transparent titanium dioxide, microparticles of zinc oxide are manufactured by using sol-gel processes or precipitation in the presence of protective colloids to limit particle growth [86].

An industrial process [87] operates with solutions of zinc sulfate and zinc chloride in the ratios 1:2. Basic zinc carbonate is precipitated by feeding simultaneously the zinc-salt solution and a mixed solution of sodium hydroxide and sodium carbonate into a reactor charged with water. The precipitated product is intensively washed several times and then spray-dried.

It is used for cosmetics and paints as a transparent UV-light shielding chemical.

Trade names include Sachtotec Micro-Zinkoxid (Sachtleben, Germany) and Z-cote HP1 (SunSmart Inc., USA).

10.9.3 Zinc Phosphate [88–92]

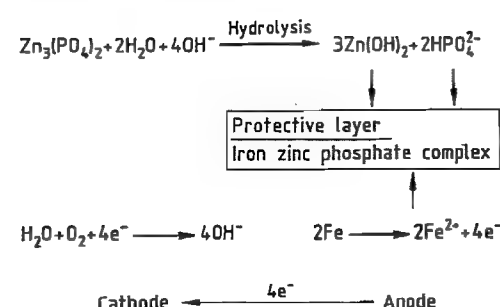
The most important phosphate-containing pigment is zinc phosphate, Zn₃(PO₄)₂·4H₂O. It can be used with a large number of binders and has a very wide range of uses [88, 89, 91–93].

Zinc phosphate is usually produced on an industrial scale from zinc oxide and phosphoric acid, or from zinc salts and phosphates [94]. Composition and properties are given in Table 10.11.

The mechanism of the action of zinc phosphate is shown in Figure 10.16. Zinc phosphate dihydrate pigment is hydrated to the tetrahydrate in an alkyd resin binder [95]. The tetrahydrate is then hydrolyzed to form zinc hydroxide and secondary phosphate ions which form a protective film of basic iron(III) phosphate on the iron surface [96]. The anticorrosive action of zinc phosphate depends on its particle size distribution. Micronization improves the anticorrosive properties [97–99].

Table 10.11: Composition and properties of zinc phosphate pigments.

Property (standard)	Zinc phosphate $\text{Zn}_3(\text{PO}_4)_2 \cdot 2-4\text{H}_2\text{O}$	Micronized zinc phosphate $\text{Zn}_3(\text{PO}_4)_2 \cdot 2-4\text{H}_2\text{O}$
Metal content, % (ISO 787, part 2)	51	51
Phosphate content, % (ISO 787, part 2)	49	< 49
Chloride content, % (ISO 787, part 13)	0.01	0.05
Sulfate content, % (ISO 787, part 13)	< 0.1	0.05
Water-soluble content, % (ISO 787, part 3)	< 0.1	0.1
Sieve residue, % (ISO 787, part 18)	0.01	0.01
Density, g/cm ³ (ISO 787, part 10)	3.2	3.4
Specific surface area, m ² /g (DIN 66131/66132)	1.0	4.3
Loss on ignition, % (ISO 787, part 2)	10–11	13
Oil absorption value, g/100 g (ISO 787, part 5)	20	24
Conductivity, μS (ISO 787, part 14)	100	300
pH (ISO 787, part 9)	6.2–7	7
Color	white-beige	white-beige

**Figure 10.16:** Passivation of iron by zinc phosphate [96].

The effect of corrosion-promoting ions on the anticorrosive properties of zinc phosphate is described in [100, 101].

Trade names are as follows:

Zinc phosphate: Sicor ZNP/M, ZNP/S (BASF, Germany); Heucophos ZP10 (Dr. H. Heubach, Germany); Halox Zinc Phosphate (Halox Pigments, USA); Phosphinox PZ20 (SNCZ, France); Hispafos N 2 (Colores Hispania, Spain).

Basic zinc phosphate: Heucophos ZPO (Dr. H. Heubach, Germany); HispafosSP (Colores Hispania, Spain).

10.9.4 Zinc Hydroxyphosphite

Commercial zinc hydroxyphosphite is a white, nontoxic pigment with basic character.

The pigment has the following physical properties [102]:

Oil absorption value, g/100 g	15–20
Density, g/cm ³	3.96
pH, 2% suspension	6.5–7.5
Mean particle size, μm	2–3

Water-soluble content, g/100 cm³ < 0.01
Specific conductivity, Ω/cm 9700

A *trade name* for zinc hydroxyphosphite is Nalcin 2 (National Lead Chemicals, USA; Kronos Titan, Germany).

10.9.5 Zinc Cyanamide

Zinc cyanamide, ZnCN_2 , is a white to beige powder which has the following properties [103]:

Density, g/cm ³	ca. 3.1
Apparent density, g/cm ³	ca. 250
Metal content, %	ca. 60
CN ₂ content, %	ca. 34
Specific surface area, m ² /g	ca. 50
pH	8.5
Conductivity, μS	< 1000

10.9.6 Zinc and Calcium Ferrites

Many paint formulations contain iron oxide as an extender. It is a physically protective anticorrosive pigment (only to a small extent). In order to obtain a chemically protective anticorrosive pigment with active constituents the iron oxide is heated with oxides or carbonates of alkaline earths (CaO , CaCO_3) or zinc (ZnO) to form pigments of the ferrite type [104, 105]. The following systems have been reported for alkyd resin primers: $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, and $\text{Zn}(\text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3$. In the coating these pigments are hydrolyzed with water to form alkaline-earth hydroxides or zinc hydroxide which prevent corrosion by increasing the pH. Alkaline-earth soaps are also formed in certain binder media [106]. However, the

pigment volume concentration must be high to ensure good results [107].

Only one zinc ferrite pigment has attained economic significance. Its properties are as follows [108]:

Water-soluble salts, %	max. 0.6
Oil absorption value, g/100 g	ca. 22
pH	9–11
Density g/cm ³	5.0

A *trade name* for zinc ferrite is Anticor 70 (Bayer, Germany; Mobay Chemical Corporation, USA).

10.9.7 Zinc Dust

Zinc dust, *mp* 419.4 °C, density 7.14 g/cm³, is a free-flowing blue-gray powder composed of spheroidal particles. It is produced by melting zinc in a crucible, vaporizing it at ca. 900–950 °C, and condensing and sifting the product. Alternatively, molten zinc is atomized with a nozzle to produce dust, which is then sifted. Properties of commercial zinc dust pigments are listed in Table 10.12 [109, 110].

Table 10.12: Properties of commercial zinc dust pigments.

Property	Zinc dust Ultra 25	Zinc dust Ultra 35
Total zinc content, %	> 99.0	> 99.0
Metallic zinc content ^a , %	94–96	94–96
Lead content, %	< 0.005	< 0.005
Cadmium content, %	< 0.005	< 0.005
Iron content, %	0.003	0.003
Copper content, %	0.001	0.001
Acid-insoluble material, %	< 0.1	< 0.1
Sieve residue ^b , %	< 0.01	< 0.01
Mean particle size ^c , μm	2.8–3.2	3.3–3.8

^a KMnO_4 method.

^b Sieve residue on 16 900 sieve (DIN 4188, aperture: 45 μm).

^c Air permeability method.

The action of zinc dust in primers with organic binders is based on sealing effects and electrochemical processes. The zinc reacts with water and atmospheric oxygen that diffuse into the binder, forming zinc hydroxide which is then neutralized by sulfuric acid (from SO_2 in the air) and hydrochloric acid (from Cl-containing substances in the air, e.g., NH_4Cl). This causes an increase in volume and decreases permeability. The corrosion products of zinc also have an anticorrosive ac-

tion [111]. Cathodic protection takes place when the zinc and iron come into contact; the zinc content in the primer must be at least 94–96% [112–115]. Zinc dust coatings are used in large quantities for structural steel, including underwater steel construction and shipbuilding. Zinc dust is also used in inorganic binder systems (alkali silicates or alkyl silicates) in the form of two-component systems [116].

A *trade name* is Zinc Dust Ultra 25' and 35 (Lindgren & Söhne, Germany).

10.9.8 Flake Zinc Pigments

Flake zinc pigments are used mainly as high-quality anticorrosive pigments in powder or paste form. Owing to their platelet structure they have a considerably higher surface area than spherical zinc dust particles. They can therefore take up much more binder which produces a more flexible coating film than that obtained with zinc dust. Other advantages include a lower settling tendency, good remixing, and problem-free application onto the precoated surface.

The flake zinc pigments give a considerably brighter, better metallic effect than zinc dust. Their appearance can be further improved by combining them with aluminum pigments or by applying a topcoat based on aluminum pigment.

Another widespread application for flake zinc pigments is the coating of small articles with complex shapes (e.g., screws, steel springs, bolts, rivets) and for special anticorrosive paints.

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11 Tin

GÜNTER G. GRAF

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11.1 History [1-4, 6, 11, 15]

Because of its luster and softness, tin was usually assigned to the planet Jupiter, more rarely to Venus. The name of the element is derived from the Old High German *zin* and the Norse *tin*. The symbol Sn from the Latin *stannum* was proposed by BERZELIUS. Historically tin is of major cultural importance, being an essential component of the copper alloy bronze which gave its name to the Bronze Age. The first bronze objects appeared in Egyptian tombs dating from the end of the 4th millennium B.C.

Pure tin was first produced in China and Japan around 1800 B.C. Around 600 B.C., the ancient Egyptians occasionally placed pure tin artifacts in mummies' tombs. Tin is not only an essential constituent of tin bronze, but is also a constituent of lead alloys for solders and tin plating. Tin and especially its alloys have shaped the development of many geographical

regions, e.g., China, Indochina, Indonesia, India, the Near East, North Africa, and Europe.

The cultural and historical importance of tin from the Middle Ages to early modern times lay in its use for sacred objects, articles of daily use, and jewelry.

There is no historical evidence concerning the oldest methods of tin extraction. It is fairly certain that in 100 B.C. in Cornwall, England, tin was smelted from very pure ore over wood fires in pits and later in small furnaces. Up to the 1200s, Cornwall provided most of Europe's tin. Today, these deposits are virtually exhausted. Tin was probably produced in Bohemia around 1150. Also, the first tin mines were opened in Saxony at this time, and these supplied European requirements until they were destroyed in the Thirty Years War. Then, as these various deposits gradually became exhausted and as ocean transport developed, tin from overseas became dominant.

The largest tin mines are in Asia, the most important ore-supplying countries in the world being Malaysia and Indonesia, followed by China. The second largest tin-producing region includes Brazil and Bolivia. The countries exporting the largest quantities of tin ores also produce the most tin metal. World annual production has developed as follows:

ca. 1800	9 100 t
ca. 1850	19 000 t
ca. 1900	91 900 t
ca. 1950	172 100 t
1980	243 600 t
1990	225 600 t

The principal consumer countries are the United States, Japan, China, and Russia.

11.2 Properties

Physical Properties [1, 2, 4, 16–19, 20]. Tin, Sn, exists in two crystalline modifications, the α - and β -forms. A third modification may also exist. Some physical properties of α - and β -tin are listed in the following:

Natural isotopes	10
Relative atomic mass	118.69
Crystal structure	
α -Sn (gray tin)	fcc (A_4) diamond type
β -Sn (white tin)	tetragonal (A_2)
Transformation temperature	
α -Sn \leftrightarrow β -Sn	286.2 K
Enthalpy of transformation	1966 J/mol
Lattice constants at 25 °C	
α -Sn	$a = 648.92$ pm
β -Sn	$a = 583.16, c = 318.13$
Density of β -tin at 20 °C	7.286 g/cm ³
100 °C	7.32
230 °C	7.40
Density of α -tin	5.765 g/cm ³
Density of liquid tin at 240 °C	6.992 g/cm ³
400 °C	6.879
800 °C	6.611
1000 °C	6.484
Molar heat capacity of β -tin	
25 °C	27.0 J/mol ⁻¹ K ⁻¹
230 °C	30.7
Liquid	28.5
Melting point	505.06 K
Enthalpy of fusion	7029 J/mol
Boiling point	2876 K
Enthalpy of vaporization	295 763 J/mol
Vapor pressure at 1000 K	9.8×10^{-4} Pa
1800 K	750
2100 K	8390
2400 K	51 200
Cubic coefficient of expansion	
α -tin at -130 °C to +10 °C	$(14.1 \text{ to } 4.7) \times 10^{-6}$ K ⁻¹
β -tin at 0 °C	59.8×10^{-6}
β -tin at 50 °C	69.2×10^{-6}

β -tin at 100 °C	71.4×10^{-6}
β -tin at 150 °C	80.2×10^{-6}
Molten tin at 700 °C	105.0×10^{-6}
Coefficient of thermal conductivity of β -tin at 0 °C	0.63 W cm ⁻¹ K ⁻¹
Surface tension at 232 °C	0.53–0.62 N/m
400 °C	0.52–0.59
800 °C	0.51–0.52
1000 °C	0.49
Dynamic viscosity at 232 °C	2.71×10^{-3} Pa·s
400 °C	1.32×10^{-3}
1000 °C	0.80×10^{-3}
Specific electrical resistivity	
α -tin at 0 °C	5×10^{-6} Ω m
β -tin at 25 °C	11.15×10^{-6}
Transition temperature for superconductivity	3.70 K
Magnetic susceptibility of β -Sn	2.6×10^{-11} m ³ /kg

In the periodic table, tin lies on the boundary between metals and nonmetals. The transformation of the α - to the β -modification is accompanied by a complete change of lattice structure, affecting the physical, chemical, and mechanical properties. Also, at 170 °C there is a second-order transformation accompanied by a discontinuous change in the lattice parameters and thermomechanical properties. A tetragonal high-pressure modification of tin, stable between 3500 and 11 000 MPa, is described in the literature the lattice constants being $a = 381$ pm and $b = 348$ pm.

The transformation of β -tin (white tin) into α -tin (gray tin) is of practical importance, as it involves a volume increase of 21%. The transformation process requires a high energy of activation, and can be very strongly hindered. White β -tin can therefore exist for many years at -30 °C. The presence of α -tin seed crystals is important for the transformation process, and these are formed by repeated phase transitions. Foreign “elements” also affect the transformation temperature and rate. These can consist of impurities and deformations. The effect of impurities on transformation behavior is described in [21]. Tin vapor consists of Sn₂ molecules.

Mechanical properties [1, 2, 4, 20–23] are not of great relevance to most applications of pure tin. The most important are listed in the following:

Yield strength at 25 °C	2.55 N/mm ²
Ultimate tensile strength at -120 °C	87.6 N/mm ²
15 °C	14.5
200 °C	4.5

Brinell hardness	
(10 mm, 3000 N, 10 s) at 0 °C	4.12
100 °C	2.26
200 °C	0.88
Modulus of elasticity E at -170 °C	65 000 N/mm ²
-20 °C	50 000
0 °C	52 000
40 °C	49 300
100 °C	44 700
200 °C	26 000

Chemical Properties [1, 2, 4, 20]. Tin has the atomic number 50 and is a member of group 14 of the periodic table. The electronic configuration is $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^4 d^{10} 5s^2 p^2$. Tin can be di- or tetravalent. It is stable in dry air, but is considerably more rapidly oxidized at a relative humidity of 80%. Bright metallic tin becomes dull within 100 d even in indoor atmospheres. Oxygen is rapidly and irreversibly chemisorbed, and the oxide layer formed grows at an exponentially increasing rate. Typical impurities present after metallurgical production (e.g., Sb, Tl, Bi, and Fe) promote oxidation. Treatment with carbonate or chromate solutions leads to passivation.

Molten tin at temperatures up to ca. 500 °C picks up oxygen from the air at a rate that obeys a parabolic law, a result of the compact layer of oxide formed.

Gaseous water and nitrogen do not dissolve in solid tin. Dissolution in molten tin only occurs at high temperatures (ca. > 1000 °C). Under the conditions of electrochemical reduction in hydrochloric acid solutions, atomic hydrogen forms SnH₄, and elemental nitrogen forms Sn₃N₄.

Tin is stable towards fluorine at room temperature, but SnF₂ or SnF₄ are formed at higher temperatures.

Rapid and vigorous reactions occur with chlorine, bromine, and iodine, these reactions being accelerated by moisture and elevated temperatures. The reaction products are SnCl₄, SnBr₄, SnI₂, and SnI₄.

Sulfur reacts rapidly with molten tin at > 600 °C to form the sulfides SnS, Sn₂S₃, and SnS₂. The reaction rate is lower above 900 °C, and only SnS is formed.

Reaction with hydrogen sulfide is slow and only occurs in the presence of oxygen and moisture. Sulfur dioxide reacts with molten tin

to form SnO₂ and S, and a molten solution of tin in copper reacts with SO₂ to form SnO₂ and Cu₂S (an important reaction in pyrometallurgy). Tin is stable towards pure hot water, steam, and dry ammonia. Nitrogen oxides only react with molten tin.

Tin is amphoteric, reacting with both strong bases and strong acids with evolution of hydrogen. Having a normal electrode potential of -0.136 V, tin lies between nickel and lead in the electrochemical series.

With sodium hydroxide solution, tin forms Na₂[Sn(OH)₆], and with potassium hydroxide solution K₂[Sn(OH)₆].

Tin reacts slowly with acids in the absence of oxygen. The high hydrogen overvoltage is caused by a layer of atomic hydrogen at the metal surface preventing further attack. Vigorous reactions occur with nitric acid, the rate depending on the acid concentration. The reactions are very vigorous with 35% acid, but complete passivation can occur at concentrations > 80%. Tin is stable towards fuming nitric acid. While hydrogen fluoride does not attack tin, hydrochloric acid reacts even at a concentration of 0.05% and temperatures below 0 °C. Tin is not attacked by sulfurous acid or by < 80% sulfuric acid.

The most important use of tin and tin-plated materials is in the preserved food industry. For this reason, the possibility of reactions of tin with certain organic acids is important. Lactic, malic, citric, tartaric, and acetic acids either do not react at all at normal temperatures or do so to a negligible extent, especially in the absence of atmospheric oxygen. This is also true of alcohols and hydrocarbons.

11.3 Occurrence, Ore Extraction, and Beneficiation

The average concentration of tin in the earth's crust is estimated to be 2–3 ppm, comparable to cerium and yttrium. Owing to the high atomic mass of tin and the high density of its important minerals, its volume concentration is very low. However, it occurs in only a small number of locations, where conse-



quently its relative abundance is high. In general, 1000-fold enrichment is necessary to give workable tin deposits, i.e., with a tin content of at least 0.2%. The question of whether a deposit can be economically extracted, for a given world market price level, depends on the mining conditions. For example, there are deposits in Bolivia containing 1% Sn which cannot be economically extracted, whereas in South East Asia placer deposits containing 0.02% Sn are successfully mined.

11.3.1 Minerals

Native tin occurs only very rarely and has only been identified with certainty in Canada.

Cassiterite, SnO_2 , is the most economically important tin mineral. It forms tetragonal crystals, has a Mohs hardness of 6–7, a density of 6.8–7.1 g/cm³, and a tin content of up to 79%. The color is usually brown to brownish black. The presence of Ti, Fe, Nb, Ta, or Mn can lead to colors varying from gray to white. Contact deposits of cassiterite can be combined with, e.g., magnetite, arsenical iron pyrites, or zinc blende. Placer deposits of cassiterite are of major importance. "Wood tin" consists of gel-like or very fine grained aggregates of cassiterite. Cassiterite is an oxidic mineral and is chemically very resistant, in particular towards weathering.

Stannite (bell metal ore), $\text{Cu}_2(\text{Fe}, \text{Zn})\text{SnS}_4$, forms tetragonal crystals, has a Mohs hardness of 4, a density of 4.4 g/cm³, and a tin content of up to 27.6%. Its color is steel gray with an olive green tinge. It is chemically less resistant than cassiterite, seldom occurs in hydrothermal deposits, and is of little economic importance.

Hydrocassiterite (varlamoffite), H_2SnO_3 , is a tetragonal gel-like stannic acid. It occurs in Bolivia, usually accompanying cassiterite.

Other tin minerals include teallite, $(\text{Sn}, \text{Sb})\text{S}$; herzenbergite, SnS ; franckeite, $\text{Pb}_5\text{Sn}_3\text{Sb}_2\text{S}_{14}$; cylindrite, $\text{Pb}_3\text{Sn}_4\text{Sb}_2\text{S}_{14}$; thoreauite, SnTa_2O_7 ; hulsite, (iron tin borate); and stokesite, $\text{CaSn}(\text{Si}_3\text{O}_9) \cdot 2\text{H}_2\text{O}$. None are of economic importance.

Table 11.1: Tin ore reserves and mine outputs for various countries in 1990.

Country	Ore reserves (t metal content)	Output (t metal content)
Malaysia	1 200 000	28 500
Thailand	1 200 000	14 600
Indonesia	1 550 000	31 700
Bolivia	980 000	17 300
Russia	1 000 000	13 000
China	1 500 000	35 800
Australia	330 000	7 400
Brazil	400 000	35 100
Zaire	200 000	1 600
United Kingdom	260 000	3 200
South Africa	50 000	1 100
Nigeria	280 000	200
Others	765 000	17 000
<i>World total</i>	<i>9 715 000</i>	<i>210 700</i>

11.3.2 Deposits

The economically important tin deposits are closely associated with acidic to intermediate magmatic rocks which were formed in the orogenic phases of the earth's history. Tin, a volatile metal, was deposited primarily during the pegmatitic, pneumatolytic, or hydrothermal phase in the region of the exo- or endocontact of the intrusive bodies. The economically much more important secondary tin deposits exist as eluvial, alluvial, or marine placer deposits which can be near to or remote from these acidic magmatic rock complexes. An overview of the ore reserves and of the amounts extracted in 1990 is given in Table 11.1.

Primary deposits originate from the pegmatitic formation of cassiterite in contact with granites or their secondary rocks. Cassiterite occurs there in idiomorphic pyramidal crystals of > 2 mm diameter. These tin-bearing granites and pegmatites typically include the minerals quartz, albite, potassium feldspar, muscovite, and cassiterite. Columbite is an important accompanying mineral. Deposits of this type are found in central and southern Africa, Brazil, and Russia (Siberia). They account for < 5% of world production. Cassiterite quartzes of the pneumatolytic catathedral phase were formed in vein fissures of granites and their secondary rocks. Individual veins or lodes can have a tin content

of up to 3%. They can be 0.2–1 m thick and up to 200 m deep.

There are various types of paragenesis of the granites, leading to the greisen type (mica-feldspar-quartz formed by pneumatolysis with fluor spar, lepidolite, and tourmaline), the topaz-quartz type, the feldspar-quartz type, and the quartz type. Such deposits contain ca. 20% of the world's tin reserves, and are found in Malaysia, Russia (Siberia), and Germany (Erzgebirge in Saxony). Cassiterite-sulfide deposits of the hydrothermal phase are formed as vein ores associated with intrusions of granodioritic rocks, or are formed by remigration of the metal content of older pegmatitic tin deposits caused by younger acidic subvolcanoes. Characteristic of these types of deposit is the paragenesis of cassiterite with stannite, iron pyrites, arsenical iron pyrites, galena, zinc blende, magnetic iron pyrites, and copper sulfides. These deposits, which can be very large, are mined in Bolivia, Russia, southern China, Thailand, Burma, Australia, South Africa, and also England. They constitute ca. 15% of the world's tin reserves.

Because cassiterite is resistant to weathering and is hard and dense, the weathering of the primary tin-bearing rocks enables it to become concentrated as it is transported to form secondary deposits, i.e., eluvial, deluvial, or marine placers.

Alluvial placers are formed by intense weathering and breakdown of cassiterite-containing granites or granodiorites, especially under tropical climate conditions. The lighter minerals are washed out or carried away by wind, while the cassiterite and other heavy minerals remain behind and can become concentrated in deposits of considerable thickness, as in Malaysia and Zaire. Very coarse and deluvial placers are also formed by gravitational enrichment due to landslips and eluviation at the bottom of mountainsides.

Alluvial or fluviatile placers are formed by the transport of weathered tin-bearing rocks by flowing water derived from atmospheric precipitation. The softer and lighter components of the rock are more extensively size reduced and therefore transported further than

the hard, resistant cassiterite minerals, which sink due to their high density and are deposited at points where flow rates are low. The most important alluvial placer deposits are in central Africa (Zaire, Rwanda), western Africa (Nigeria, Niger), and Brazil. Marine placers are formed where primary tin-bearing rock complexes have been directly transported by surf, or where rivers have carried the cassiterite-containing sediment into the sea, where it is then deposited in coastal strips. These are the most important deposits, and represent ca. 60% of the world's workable reserves. The largest of these deposits are in south-east Asia, the coast of Thailand, the Thai Island of Phuket, in Malaysia, and on the Indonesian Islands of Bangka and Billiton.

Secondary deposits usually have tin contents of 0.05–0.5%, reaching 3% in some cases. Marine placers have tin contents of 0.01–0.03%. At present, deposits containing 0.1% Sn are workable by the open-pit method. For underground mining, deposits should contain 0.3% Sn.

11.3.3 Mining

Primary tin ores are extracted by underground mining. Depths can reach 1000 m in exceptional cases. Most of the technologies used in nonferrous metal mining are used, the method in a given situation being determined by the thickness, shape, and orientation of the ore body, and geological factors.

In secondary deposits, the loosely packed weathered hard mineral rock which contains the cassiterite together with associated deposits of sand and gravel is extracted by high-production loading techniques which also perform preliminary classification. General local conditions, including the state of economic development in the region, have a great influence on the mining conditions. For example, in Zaire, surface eluvial deposits (weathered pegmatites) with tin contents of up to 0.15% are extracted by conventional open-pit methods. In Thailand, Malaysia, and Indonesia, loose alluvial and marine deposits in river valleys and in the undersea regions just off the

coast are extracted by dredging shovels, dragline excavators, chain and bucket excavators, and similar equipment specially designed for local conditions. The initial separation of gangue and other foreign materials (e.g., wood) is performed by this equipment. Cassiterite in thick deposits of loose sediments and coarse detritus in Southern China and Thailand is treated with powerful water jets operating at pressures of up to 1.5 MPa. These generate a mixture of water and heavy sand which is then fed to the treatment plant.

Off the coasts of Indonesia, Thailand, and Malaysia, chain and bucket excavators are used to extract cassiterite from alluvial deposits under water at depths of up to 40 m. This also gives a preliminary beneficiation.

11.3.4 Ore Beneficiation [11, 24–28]

The beneficiation of primary tin ores is difficult. The principal mineral, cassiterite, is nonmagnetic and is not suitable for flotation, so that mainly gravimetric sorting processes must be used. Furthermore, cassiterite is often strongly intergrown, and the accompanying minerals behave similarly to cassiterite during processing.

Current technologies are characterized by controlled multistage size reduction of the ores and separation of the cassiterite released after each size reduction stage using sorting methods based on density. Screen jigs and shaking tables of various designs are used. However, very small particles (< 30 μm) cannot be processed to give satisfactory yields and production rates. If the degree of intergrowth of the ores requires finer grinding, as is increasingly the case with ores from Russia, the United Kingdom, Bolivia, South Africa, and Portugal, the flotation method for sorting particles < 100 μm is sometimes used. This technique was also used for the tin ore from the Altenberg region of Saxony, whose mines were closed in 1990. The following stages of beneficiation of primary tin ores are used:

Ores with an average degree of intergrowth are concentrated mainly by processes based on density. Flotation is increasingly used to sort

fine-grained material and ground middlings obtained by the density-based sorting process, and has now become the preferred method for treating the most finely intergrown, complex tin ores. Flotation of cassiterite with particle sizes between 40 and 10 μm is mainly carried out with arsonic acids.

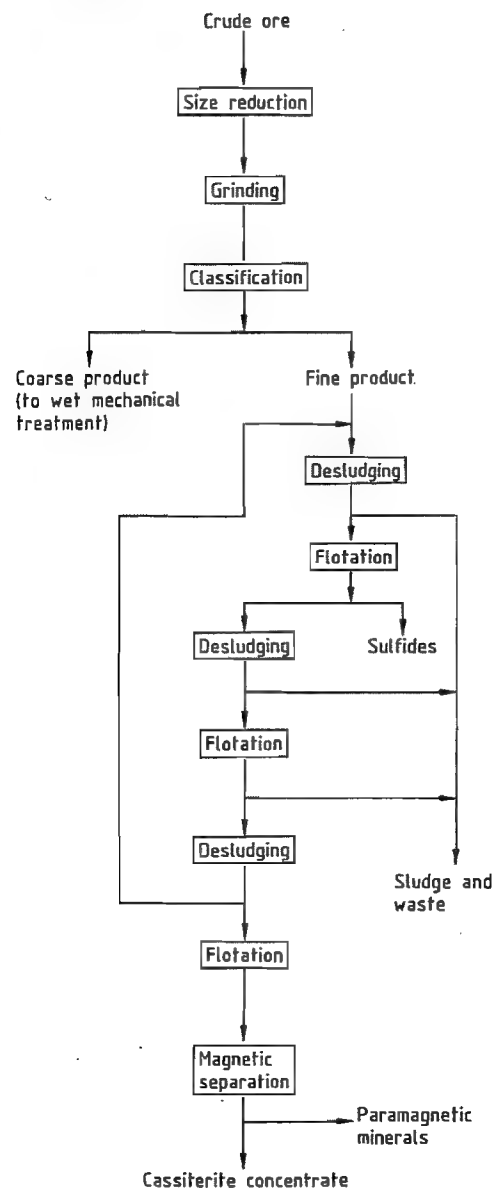


Figure 11.1: Flotation of primary tin ores.

The flow diagram (Figure 11.1) shows the flotation of primary tin concentrates to remove sulfides of similar paragenesis, followed by flotation of cassiterite from the preconcentrate, and magnetic separation of paramagnetic minerals from the flotation product.

Composition ranges for complex tin concentrates are:

Sn	5.6–60%
S	1.0–15%
As	0.1–3%
Sb	0.1–2%
Bi	0.1–0.5%
Cu	0.1–0.7%
Pb	0.1–3%
Zn	0.1–4%
Ag	up to 500 ppm
W	0.1–5% WO_3
Nb/Ta	1–3% $\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$

The ores from placer deposits are thoroughly broken down by natural weathering processes which separate the material roughly according to the rate at which it settles out of suspension. The fine-grained cassiterite is mixed with coarser sand or gravel. On board the floating dredges, which operate in artificial dredging ponds or natural surface waters, there is ore beneficiation equipment which produces a preconcentrate for further processing on shore (Figure 11.2). The ore passes through a drum screen which removes coarse gravel (10–20 mm), wood, and other foreign bodies. The material passing through the screen is desludged in a hydrocyclone, and treatment on a three-stage screen jig then produces heavy metal concentrate for further processing on shore.

The ore obtained from placer deposits on land using water cannons or from the seabed using special ships with suction pumps is processed using conventional ore beneficiation methods such as screen jigs or screen troughs.

Concentrates from placer deposits are relatively pure; a typical analysis (in %) follows:

Sn	70	Ni	0.01
As	0.1	Ta_2O_5	0.2
Sb	0.05	Nb_2O_5	0.1
Pb	0.008	WO_3	0.05
Cu	0.005	SiO_2	5.0
Zn	0.01	CaO	0.1
Bi	0.015	TiO_2	0.1
Fe	0.3	Al_2O_3	1.0

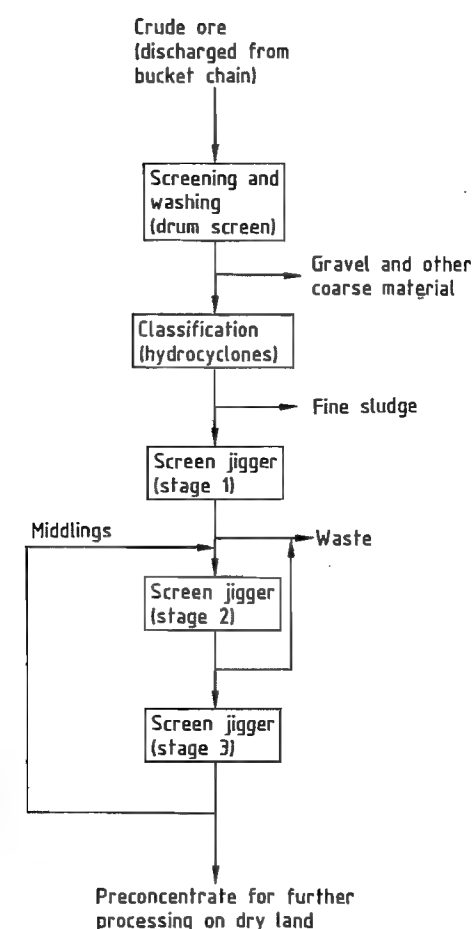
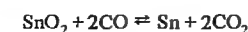


Figure 11.2: Preparation of secondary tin ores (placer deposits) on floating dredgers.

11.4 Smelting

11.4.1 Fundamental Theory of Smelting [1–3, 5, 29–34]

Because the most important tin-bearing mineral in tin ore is cassiterite (SnO_2), the carbothermic reaction



is of fundamental importance.

A theoretical consideration of tin smelting must include the temperature dependence of this equilibrium and the behavior of the im-

portant reactants (Sn, O, and C) and accompanying elements and impurities in the concentrate, e.g., Fe, Cu, Sb, Bi, Ag, Si, Ca, Al, Mg, Nb, Ta, etc., of which Fe is the most important. The equilibrium diagrams for Sn-O-C and Fe-O-C are of crucial importance in the reduction of tin. At temperatures above 1100 °C, not only the Sn but also the Fe present in the oxidic precursors is reduced, so that selective winning from industrial tin-containing raw materials, which always also contain iron, is impossible. Furthermore, in this temperature range, up to 20% tin dissolves in iron, and iron-tin compounds (known as hard head) are formed at lower temperatures, so that iron-free tin cannot be obtained under these conditions. This restricts the advantage of using a high process temperature to give a faster reaction rate in carbothermic cassiterite reduction. Also, the technique of stably binding iron in fayalite, to enable tin reduction to be carried out selectively, though realized on a laboratory scale by WRIGHT [29], could not be scaled up to production conditions.

The elements involved in tin reduction can be divided into the following groups:

- Elements more noble than tin are reduced at lower temperatures than tin, and dissolve in molten tin (e.g., Cu, Pb, and Sb)
- Elements that are much less noble than tin and which are not reduced under the reduction conditions, but which act as important slag formers, such as Ca, Al, and Si in the form of their oxides
- Iron, the most important accompanying element, which behaves similarly to tin
- Gaseous compounds produced in the reduction process
- Sulfur, which has an important role in the reduction and volatilization process of pyrometallurgical tin production

Both the iron and the slag formers must be removed in a liquid slag; this determines the minimum process temperature. The iron content of the metal product depends on the Fe/Sn ratio in the slag. This relationship, represented in Figure 11.3, illustrates the principal problem of tin production from oxidic raw materi-

als. If a high tin yield is to be obtained, i.e., small losses of tin in the slag (e.g., < 10%), high reduction temperatures must be used, giving an iron content in the tin of > 8%, so that subsequent refining is more difficult. If a purer metal is desired (e.g., 0.5% iron in the tin), there will be high losses of tin in the slag, whose tin content can be 10–25%. These slags are starting materials for a second process stage.

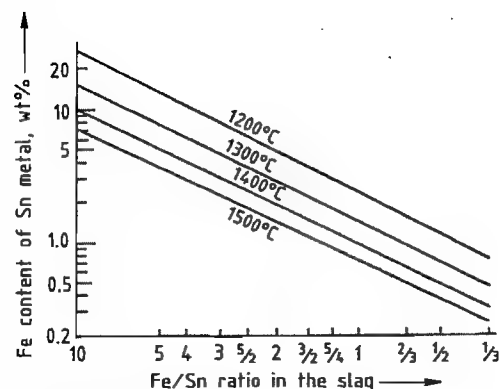
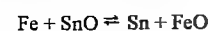


Figure 11.3: Calculated Fe/Sn ratios in the metal and slag at equilibrium as a function of temperature.

The reactions in the slag phase are of major importance for selective reduction, whereby SnO is an important component. Experiments on pure substances have shown that although SnO melts at 980 °C it is unstable below 1100 °C, decomposing into SnO₂ and Sn. The activity of SnO in SnO-SiO₂ melts obeys Raoult's law between 1000 and 1250 °C. The negative free energies of mixing SiO₂ with FeO, ZnO, PbO, MnO, and MgO increase in this order, and increase the SnO activities in the silicate melts. The position of the metal-slag equilibrium in the reaction



is expressed by the distribution coefficient

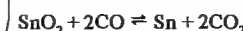
$$K = \left(\frac{\text{Sn}}{\text{Fe}} \right)_{\text{metal}} \cdot \left(\frac{\text{Fe}}{\text{Sn}} \right)_{\text{slag}}$$

K should be as large as possible, and at the usual reaction temperature of 1000–1100 °C used in tin metallurgy, should be ca. 300 to give an iron content of ca. 1% in the tin.

Binary and ternary slag systems containing tin oxides have been thoroughly investigated [33] and give useful guidance for carrying out the tin reduction. However, practical results depend very much on the viscosity of the molten products, the density differences, the surface tension, and colloidal dispersion and chemisorption of the slags. Thus, under production conditions stronger bases displace SnO bound in silicate, and FeO increases the fluidity of the slags.

The difference between the kinetics of tin oxide reduction and iron oxide reduction affects the selectivity of the reduction process and hence the iron content of the tin and the performance parameters of the furnace systems. Other important parameters are the pore structure and particle size of the raw materials, the partial pressures of the reduction gases, removal of the reaction gases, formation of seed crystals and coatings, and heat transfer. Thus, from the point of view of reaction rate, the reverberatory furnace is not the best equipment for carrying out reduction as it contains a large slow moving mass of material with a large bed thickness where heat is supplied only from above. The poor heat transfer leads to an extremely low smelting capacity, i.e., < 0.7 t metal per m³ furnace volume per day. Because slag formation is very slow, some of the tin reduced at the start of the process can be tapped off as a relatively pure, low-iron product before the entire charge is smelted.

In contrast, highly turbulent reaction systems lead to process rates orders of magnitude higher. Under practical reaction conditions above 900 °C, the reaction



is rapid, and the reaction



becomes rate determining. This is why oxygen has to be added to the mixture of solid charge and reducing carbon in the furnace.

World production of tin is two-thirds from oxidic and one-third from sulfidic raw materials. The main problem in treating sulfidic tin concentrates is their complex composition. As

many impurities as possible are vaporized in an initial roasting stage.

Arsenic requires special treatment, as it is oxidized to As₂O₃ and As₂O₅, which combines with Fe₂O₃, formed by roasting, to give non-volatile iron(III) arsenate. In practical operation, a somewhat reducing atmosphere is therefore produced by adding charcoal to the charge. Another possibility is to vaporize heavy metal chlorides by adding NaCl.

11.4.2 Special Aspects of the Winning of Tin from its Ores

Problems in ore beneficiation often lead to concentrates with low tin contents, as unacceptably high losses of material would occur if ore concentrates with higher tin contents were produced. Therefore, a pyrometallurgical "thermal ore beneficiation" stage is necessary prior to the actual reduction process. This is a volatilization process that exploits the fact that the iron compounds and other slag formers have low vapor pressures at 1000–1500 °C, while SnO and SnS volatilize very readily. This technique can also be used to treat tin-containing slags.

The vapor pressure of SnS is considerably higher than that of SnO. Therefore, in practice, SnS is vaporized and then oxidized to SnO and SO₂. Pyrite (FeS₂) added as sulfur source causes problems in later stages of the process, as the FeO formed must be slagged, and the SO₂ evolved makes waste-gas cleaning necessary. However, this is outweighed by the advantages of a high yield of tin at relatively low process temperatures.

Economic advantages can be achieved by using cheap sulfur-containing grades of heating oil as fuel in the roasting process.

The naturally occurring ore beneficiation process that takes place in cassiterite deposits in surface waters and the increasing use of ore concentration processes with finely intergrown ores lead to extremely fine grained materials. Processes of agglomeration or compaction would be very costly. For this reason, these types of raw material are usually treated in an ore reverberatory furnace.

The main problem in pyrometallurgical tin production processes is separating tin from iron. Under production conditions, simultaneous reduction of SnO and FeO cannot be prevented. Molten tin can dissolve large amounts of iron, and intermetallic compounds, which are very difficult to separate, can be formed on solidification. To minimize this problem, tin production is carried out in two stages. In the first stage, under mild reduction conditions, a relatively pure tin and a rich slag are produced. The latter is treated under strongly reducing conditions in the second stage, giving a discardable slag and a very impure tin-iron compound. The metallic phase is returned to the first stage, where the iron is re-oxidized. The two-stage process must be carried out such that the iron initially in the concentrate is eventually removed from the process in the waste slags.

11.4.3 Production of Crude Tin

11.4.3.1 General Aspects

The choice of a crude-tin production process involves consideration of factors associated with both raw materials and location, and the following questions must be posed:

- Whether the raw materials are highly enriched concentrates with low levels of impurities
- Whether the raw materials used are low-grade concentrates whose principal impurities are slag components
- Whether complex raw materials containing at least one other valuable element (e.g., W, Nb, or Ta) are used

Other important factors include the availability of raw materials, energy costs, environmental considerations, and personnel costs.

11.4.3.2 Ore Preparation prior to Reduction

As a result of the problems described in Section 11.3.4 and also of the efforts to recover as much of the tin from the ore as possi-

ble, the tin content of the ore concentrate can range from 8 to 60%. Hence in most cases, pretreatment is necessary, e.g., pyrometallurgical enrichment of low-grade raw materials, a roasting stage (sometimes with addition of fluxes), or a leaching operation.

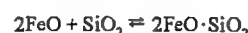
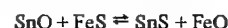
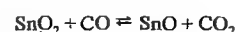
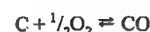
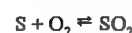
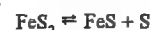
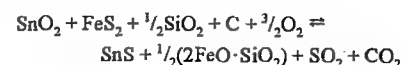
Pyrometallurgical Enrichment of Low-Grade Concentrates [1-5, 28-30, 34-41]

Low-grade tin concentrates are subjected to pyrometallurgical enrichment. The tin is vaporized as sulfide, and then oxidized in the gas phase by atmospheric oxygen to form SnO₂. The nonvolatile components of the raw material are selectively removed, and with careful process control, 90-95% of the tin can be recovered as an oxidized product containing 40-60% Sn.

Optimum results are only obtained if the reaction of the sulfide with oxygen takes place exclusively in the gas phase; therefore, reducing conditions must be maintained in the furnace. Although gaseous sulfur is the best sulfiding agent from a thermodynamic viewpoint, pyrites is used almost exclusively under production conditions. If calcium sulfate is used, the disadvantage that energy is required for its dissociation must be balanced against the advantage that the CaO produced is a useful slag former.

Although the vaporization of tin as SnS is used in all production plants, there is no generally accepted model of the reactions that take place. However, it is probable that in view of the S/Sn ratios required, the available polysulfidic sulfur in the pyrites does not take part in the formation of tin sulfide. Furthermore, it can be deduced from the importance of the added carbon to the reaction product obtained and from the CO content or oxygen demand of the reaction gases that SnO₂ is reduced first to SnO in an intermediate stage and SnS is then formed by the reaction of SnO with FeS. This is supported by the fact that the pyrites or the FeS formed therefrom forms SnS more readily than does sulfur vapor, contrary to what would be expected from thermodynamic considerations.

These results, especially when supported by practical experience, show that the overall equation and the individual reactions are probably as follows [28]:



Pyrometallurgical enrichment of low-grade tin concentrates can be carried out in various types of furnace.

Initially, rotary and shaft kilns were used for the vaporization process. Although the operation of both types of equipment was technically sophisticated, there were considerable disadvantages, which eventually led to their abandonment. Apart from the high energy and fuel requirements typical of both systems, the shaft kiln process led to a relatively low direct yield of tin in the flue dust, mainly due to the production of matte, which required separate processing. The rotary kiln method led to a low tin concentration in the flue dust, and, for raw material of high iron content, to the formation of matte, and hence to a drum clinker, which had then to be processed in a shaft kiln.

High-capacity thermal concentration processes, already established on a large scale in the nonferrous metal industry, were therefore adapted to tin enrichment. The fluidized bed and the cyclone smelting processes were not used. Also, the flash smelting (levitation smelting) process has severe limitations because of the raw materials used. Good results could be obtained with concentrates in which most of the material had a particle size of 200-300 μm. Using such concentrates containing 10-12% Sn, discardable slags containing 0.2-0.4% Sn and flue dusts containing 50-60% Sn could be obtained. On using low-grade concentrates that had not been desludged and

which contained significant amounts of material with a particle size of 50-60 μm, the amount of primary flue dust increases significantly, and the tin concentration in the flue dust sometimes decreases to < 40%. Also, the tin content of the slags is unacceptably high (1-2%).

The main disadvantage of the flash smelting process is that it imposes strict requirements on the physical form of the concentrate.

The slag blowing process, originally used for detinning the slags from the reduction process, has been increasingly used for enrichment of tin in low-grade concentrates and exploitable gangue from ore processing. These products were at first added to the initial smelting process, but they were later added in solid form directly to the blowing furnace. Smelting and blowing can be carried out in a single furnace, so that it is not necessary to build a special smelting plant. This enables capital and operating costs to be reduced.

An important part of the practical operation is the maintenance of the correct fuel-air mixture with uniform distribution of the fuel and air to the individual jets. Heating oil and natural gas are preferred because they are more easily metered than solid fuels. If pyrites is used as the sulfiding agent, an S/Sn ratio of 0.8 is necessary, which places high demands on the equipment for removing sulfur dioxide. When pyrites is used, only FeS is effective in the slag phase, so that only 50% of the sulfur is used for sulfiding. If pyrrhotite (magnetic pyrites) or calcium sulfide is used, the S/Sn ratio need only be 0.4, and the emission of sulfur dioxide decreases by 50%.

The good metallurgical results of the slag blowing process, in which flue dusts containing 65-70% Sn and final slags containing 0.1% Sn are obtained, must be balanced against the disadvantage of a batch process. This leads to nonuniform loading of the downstream plant, e.g., the waste heat recovery and gas cleaning equipment.

Roasting [1, 2, 4, 5, 11, 17, 32, 42–50]

The roasting process, not only converts sulfides to oxides, but also volatilizes major oxidic impurities (e.g., arsenic). Roasting can be an independent process, or a pretreatment prior to hydrometallurgical leaching. It is significant that the level of impurities As, Sb, Pb, and Bi in tin concentrates has increased in spite of great efforts to improve ore beneficiation technology. If the levels of As and Pb are > 0.1%, and of Bi and Sb > 0.03%, a roasting process, sometimes with the addition of a leaching stage, is both useful and necessary for the benefit of the final tin reduction and refining processes.

The important reactions in the roasting process are as follows (M = metallic impurity):

- Dissociation
 $\text{FeS}_2 \rightleftharpoons \text{FeS} + \frac{1}{2}\text{S}_2$
 $4\text{FeAsS} \rightleftharpoons 4\text{FeS} + \text{As}_4$
- Roasting reactions
 $\text{MS} + \frac{3}{2}\text{O}_2 \rightleftharpoons \text{MO} + \text{SO}_2$
- Oxidation
 $\text{MO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{MO}_2$

Although the roasting reactions and especially the oxidation reactions are exothermic, addition of fuel is necessary in industrial-scale roasting processes. The pore structure of the material must be maintained to enable the gaseous metallic and nonmetallic impurities to be vaporized. The upper temperature limit for the roasting process is imposed by the melting point of the low-melting sulfide eutectic. However, the temperature should be kept as high as possible to prevent the formation of sulfates, e.g., lead and calcium sulfate.

A mildly reducing atmosphere is necessary to suppress sulfate formation and also prevent formation of higher nonvolatile oxides of the impurities (e.g., As_2O_5).

The roasting processes are carried out in multideck or rotary kilns. The use of fluidized-bed furnaces with carefully controlled operating parameters has been reported [48].

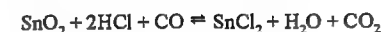
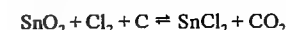
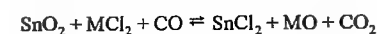
Chloridizing roasting is also suitable for the pretreatment of tin concentrates, owing to the high affinity of the main impurities for chlorine. However, problems can be caused by

chloridation of tin, which itself then volatilizes as SnCl_4 and SnCl_2 .

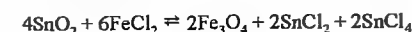
Chloridizing roasting of tin concentrates in rotary kilns is carried out in Thailand. The contents of lead and bismuth are lowered from 2.0% to 0.04%, and from 0.1% to 0.02%, respectively. The flue dust contains 10% As, 3% Sn, 20% Pb, and 4% Bi. Treatment of this product presents serious problems [2].

The processes for removing impurities by chloridation differ fundamentally from those for the volatilization of tin from concentrates, being based on the fact that a large phase field exists in the phase diagrams Sn-HCl-H_2 and Fe-HCl-H_2 between 900 and 1000 °C in which selective chloridation and volatilization of tin is possible without chloridizing iron.

The overall reactions are as follows (M = Mg, Ca, or Na):

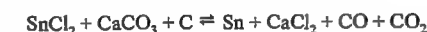
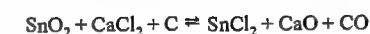


The presence of iron oxide increases yield and reaction rate, which can only be explained by intermediate formation of FeCl_2 :



Here, the instability of iron chloride in the presence of tin oxide is the reason for the good separation of tin from iron. In a reducing atmosphere, i.e., in the presence of C or CO, only SnCl_2 is formed.

In the Warren Spring process [50], CaCl_2 is used as chloridizing agent, and the CaO formed is used in the reductive smelting by adding limestone in accordance with the following equations:



The industrial-scale reaction is difficult to carry out, as moisture resulting from the hygroscopic properties of the tin chloride and the quicklime must be avoided. The corrosive properties of the reaction gases make very high demands on the construction materials used.

A special form of roasting is the heating of high-tungsten tin concentrates with NaOH or Na_2CO_3 to give soluble Na_2WO_4 , which can be leached out.

Leaching [1–4, 32, 47, 51–55]

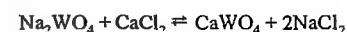
In tin metallurgy, the main use of leaching processes is to remove typical impurities from the concentrate. Tin, which is nearly always present in the raw materials as SnO_2 , can only be brought into aqueous solution if the SnO_2 is reduced to SnO in a precisely controlled CO/CO_2 atmosphere. It can then be extracted in acid or alkaline media. This procedure has not yet been operated on an industrial scale.

Only hydrochloric acid is used on an industrial scale to remove impurities by leaching, the typical impurities in the concentrate, Fe, Pb, Cu, Sb, or As, going into solution in the form of their chlorides. Best results are obtained using > 20% hydrochloric acid at 100–110 °C. Suitable reaction vessels are high-pressure, acid-resistant spherical autoclaves with a capacity of 20 t. This batch process must sometimes be repeated several times. The solids are removed by thickeners and vacuum filters, and the dissolved impurities are precipitated from the liquor by cementation on scrap iron.

The high costs of these special reactors, the batch mode of operation, and the expense of the process for recovering the hydrochloric acid have restricted the use of hydrochloric acid leaching to some special cases.

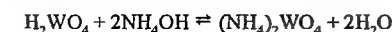
It is preferable to carry out chloridizing roasting before leaching out the impurities. This then only requires a dilute acid solution.

Leaching of tungsten-containing tin concentrates to recover tungsten is important. After digesting the ore with sodium carbonate in spherical boilers, the tungsten is converted to its hexavalent form, which is soluble in hot water. It is then precipitated from the neutral solution with CaCl_2 :



An easily filtered precipitate containing up to 60% WO_3 (on dry basis) is obtained.

Tungsten can also be extracted from tin concentrates by leaching with an aqueous solution of ammonia:



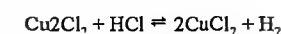
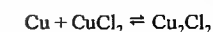
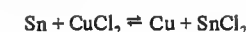
The concentration of WO_3 in the filtrate can reach 50 g/L, and this can be precipitated as artificial scheelite, $\text{Ca(WO}_4)_2$. The tungsten content of the tin concentrate can be reduced to 0.5%.

Most of the tin can be leached from a tin concentrate containing 2% bismuth with 5% hydrochloric acid at 80 °C [46].

Treatment with sulfuric acid is used to remove iron present as carbonate in Australian tin concentrates. By removing gangue material in this way, the tin content of the concentrate is increased from 37.2% to 47.1%.

A process for the removal of arsenic from tin concentrates by bacterial leaching with *Thiobacillus ferrooxidans* has been tested in Russian research institutes [54].

The tin can be leached out of ores that are difficult to treat if these are first reductively smelted with CuCl_2 and HCl, in accordance with the following series of reactions [42]:



Tin is precipitated from solution by adding zinc, and copper by adding iron.

11.4.3.3 Reduction

As explained, it is not possible to obtain high yield and high metal purity at the same time. Reduction is therefore carried out in two stages, the first stage giving a relatively pure metal (up to 97% Sn) and a rich slag (8–35% Sn). This slag is treated in a second stage, and sometimes in a third. Slag treatment processes are described later.

Various types of furnace are used for reduction. Very low grade ore in lump form can be treated in a shaft kiln. However, as most concentrates obtained in ore beneficiation are very finely divided, and agglomeration, e.g., by sintering, is impossible, other types of fur-

nace must be used in this case. Reverberatory or rotary air furnaces are often used for reduction, and electric furnaces are also employed. Each furnace type has its own advantages and disadvantages.

Reduction in a Shaft Kiln [1-3, 5, 30, 56, 57]

Shaft kilns are historically the oldest type used for tin reduction. They have their origin in the old Chinese natural draught furnaces made of rammed clay held together with wooden posts and operated on mountainsides. The hearth was usually sloped so that the molten product ran off continuously. Today, shaft kilns are water-jacketed, and have a melting capacity of $5.5-8 \text{ tm}^2\text{d}^{-1}$. The good heat transfer and the continuous method of operation give a higher melting capacity than is obtained in comparable reverberatory furnaces. The air flow rate must be low to prevent volatilization. Shaft kilns require raw material in lump form. The iron content must be as low as possible in order to limit the formation of hard head in the reducing atmosphere.

Reduction in a Reverberatory Furnace [1-3, 5, 30, 32, 58-61]

The necessity for treating fine-grained concentrates from ore beneficiation has led to the replacement of the shaft furnace by the reverberatory furnace, and this is today the most important type of reduction equipment used in tin metallurgy. Modern reverberatory furnaces have internal dimensions of 3-4 m width, 10-13 m length, and 1-1.5 m height. In a freshly lined hearth the height available for the molten charge is no more than 0.5 m. This increases with increasing wear of the furnace bottom. The bath volume of modern tin ore reverberatory furnaces is 20-50 m^3 . As the tin is very fluid at the reaction temperatures (up to 1400 °C), high pressures can be produced at the bottom of the hearth. To prevent this, either holes must be provided in the steel sheet bottom to allow the tin to drip into a lower chamber where it can solidify in stalactite

form, or the reverberatory furnace must have a water-cooled bottom so that the tin solidifies in the gaps between the bricks.

The refractory bricks and mortar used to line the furnace must be made of high-grade chrome-magnesite. This must be very pure because of possible reactions of SnO or Sn with iron oxides or silica. Chamotte can only be used above the slag zone. To avoid disturbance of the brickwork in the melting zone, charging is carried out through the roof.

The burners, which use heavy fuel oil, are situated on the narrow sides of the furnace. The furnaces operate discontinuously using the regenerative principle, the duration of a heat being 16-20 h. Specific melting capacities are in the range $1.2-2.0 \text{ tm}^2\text{d}^{-1}$. Charge batches consisting of concentrate, carbon, and fluxes weigh between 40 and 70 t. Optimum results can only be achieved by extremely careful operation.

Thus, at the start of a new heat, the amount of material charged to the furnace should be limited, e.g., by adding the charge in two portions, to prevent a large drop in temperature. The amount of carbon added in the form of coke, coal, petroleum coke, or charcoal is determined by the tin and iron contents and also by the incidence of hard head. The carbon addition is adjusted so that coreduction of the iron is prevented as far as possible.

The furnace draught must be kept low to prevent entry of cold air and to maintain the oxygen content in the waste gas below 5 vol%, thereby minimizing oxidation of the tin.

The first tin can be tapped off after 4-5 h of a 24 h cycle. As this is comparatively pure, it is preferable to treat it separately. The material tapped off later separates into metal and slag in a settler outside the smelting furnace. Some furnaces have facilities for tapping off the metal and the slag separately.

Up to 6% of the weight of charge material is converted to flue dust, which consists of entrained charge, SnO , and some SnS . Its tin content is therefore considerably higher than that in the charge material.

Compositions of products obtained when a relatively pure concentrate (> 70% Sn) is

treated in a reverberatory furnace are listed in Table 11.2. The amount of slag is relatively small (14% of the charge), but the slag must undergo a further stage of processing because of its high tin content.

A simplified flow diagram for the treatment of high-grade concentrates is shown in Figure 11.4.

The process flow diagram for low-grade, impure, and complex concentrates is considerably more complex. With high-grade concentrates, a tin yield, including that obtained from slag treatment, of 99.6% can be achieved, as actual losses of tin can only occur in the waste slag and by loss of airborne dust. In the treatment of low-grade concentrates, the yields of tin may only be 955%, and in exceptional cases 925%, because of the numerous tin-containing waste products.

Control of the CO partial pressure, which determines the reduction potential, is more

difficult in a stationary reverberatory furnace, which contains a slow-moving mass of charge, than in a shaft furnace, in which the coke and air move in countercurrent flow. This is also the reason for the poor heat transfer and hence the low rates of reduction and melting in a reverberatory furnace.

Table 11.2: Typical compositions of products from a reverberatory furnace (in %).

Component	Crude tin	Slag	Flue dust
Sn	97-99	8-25	40-70
Fe	0.02-2.0	15-40	0.8-4.0
As	0.01-2.0		0.1-0.7
Pb	0.01-0.1	0.1-0.5	0.2-1.6
Bi	0.003-0.02		0.01-0.1
Sb	0.005-0.2	0.01-0.02	0.1-0.4
Cu	0.001-0.1		0.02-0.05
Al_2O_3		7-12	≤ 1.0
SiO_2		10-30	≤ 2.0
CaO		4-14	≤ 0.6
MgO		1-4	≤ 0.6
S	0.01-0.05		≤ 1.0

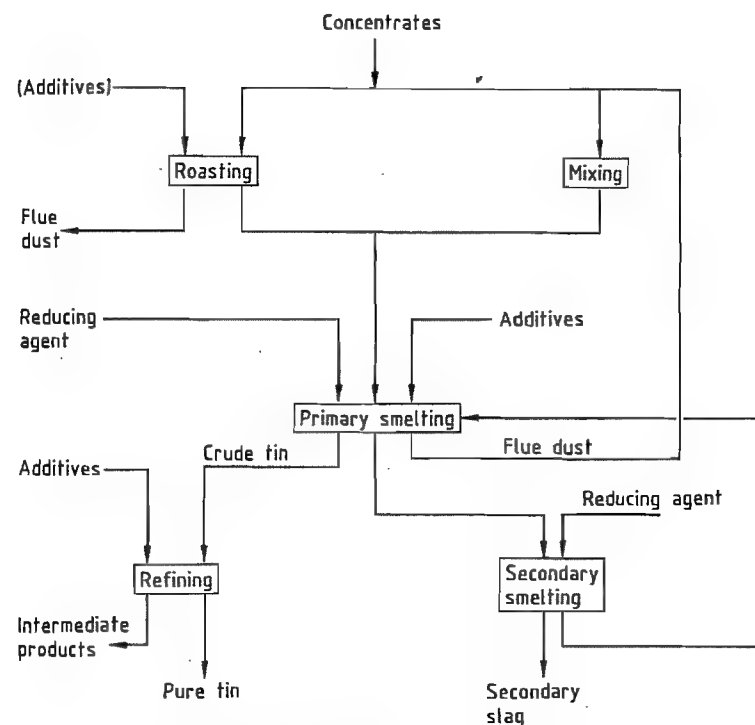


Figure 11.4: Process for treating high grade concentrates (simplified).

Under operating conditions, care must be taken that the slag formers do not melt too rapidly, as this impairs the contact between the furnace atmosphere and the unmelted charge. At the same time, the melting temperature of the slag must be as low as possible, so that the use of such slag formers as CaO and SiO₂ should be limited. Added lime is of special significance, because it displaces tin from silicate, can lead to calcium stannate formation if present in excess, and increases the melting point of the slag.

The effect of the slag constituents, especially on melting point and viscosity, is described in detail in [3]. In a process optimization/cost minimization exercise, it is always necessary to include the effect on costs of the amount of tin tied up in materials being recycled [59].

Reduction in Rotary Kilns [1–3, 5, 30, 32, 57–62]

Rotary kilns (rotary air kilns) are horizontal smelting units that operate batchwise. They have a higher melting capacity than stationary reverberatory furnaces, but lead to considerably more severe stress on the refractory lining. Operating procedures in two tin smelting works in Indonesia and Bolivia in which the reduction process is based on the rotary kiln principle are reported in the specialist literature [63]. The furnaces have a length of 8 m, a diameter of 3.6 m, a surface area of reacting material of ca. 22 m², and a specific melting capacity of 1.36–1.5 t m⁻² d⁻¹.

The furnace availability (300 d/a) is superior to that of reverberatory furnaces (260 d/a). Also, there is less requirement for mixing operations or agitation of the melt by stirring (rabbling). The metallurgical results of both types of furnace are very similar. However, the considerably poorer stability of the refractory lining, the higher energy requirement, and the significantly larger quantities of flue dust are all disadvantages. Separation of the tin from the slag has to be carried out outside the furnace in a settler.

Table 11.3: Typical compositions of products from rotary kiln at Mentok, Bangka (in %).

Component	Crude tin	Slag	Flue dust
Sn	99.78–99.83	14–25	60–72
Fe	0.089–0.144	15–26	1–4
Pb	0.010–0.031		
As	0.010–0.188		
Sb	0.005Pb.010		
Bi	0.0025–0.003		
Cu	0.002Pb.025		
SiO ₂		8–24	0.2–2.0
CaO		2–10	1–1.2
MgO		2–4	
S			0.2

Tin concentrate can also be reduced in short drum kilns in which the ratio of the length to the cross-section is 1. The metallurgical function is basically similar to that of the rotary kilns. The compositions of the smelting products in an Indonesian tin smelting works in which high-grade concentrates are reduced in a rotary kiln are given in Table 11.3.

Reduction in an Electric Furnace

[1–3, 5, 30, 32, 58, 64–68]

Electric resistance and arc furnaces used in metallurgy are characterized by high reaction temperatures and low waste-gas volumes. Disadvantages are the necessity for thorough pre-mixing of the raw materials and the batch operation. Tin smelting is often carried out in regions where electrical energy is less readily available than energy from other sources such as gas, coal, or oil. Wherever electric furnaces are used in tin metallurgy, the object is to utilize their advantages of high reaction temperature and the production of heat by the Joule effect directly in the smelting bath.

Because their reducing action is so effective, electric furnaces are particularly suitable for extracting tin from slag (see Section 11.4.3.4). In concentrates whose iron content is significantly less than 5%, it is even possible to produce crude tin in a single stage, with tin levels in the slag of < 0.7%. Electric furnaces are used in many tin smelting works for primary tin production from concentrates. These concentrates are often imported, e.g., in Germany, France, Italy, Canada, and Japan, al-

though tin concentrate producing countries, e.g., Brazil, Zaire, South Africa, Russia, Thailand, and China also use electric furnaces. The raw materials for the electric furnace process must be intensively mixed. Very fine-grained materials such as flue dust are pelletized. A moisture content of ca. 2% must not be exceeded. Typically, circular furnace vessels with an outside diameter of up to 4.5 m and a height of 1.5–3 m are used, or oval furnace vessels with dimensions 2.5 × 1.8 × 1.8 m. Heating is carried out with three-phase electric arcs using graphite electrodes. In single-phase furnaces, the furnace bottom acts as the counterelectrode for the immersed graphite electrodes.

Both stationary and tilting furnaces are used. Linings of carbon bricks give a service life of up to three years. Electric currents of 6–20 kA at 50–150 V are used. Depending on the characteristics of the raw materials, energy consumption is 750–1400 kWh/t concentrate (1300–1860 kWh/t tin). Precise control of the electrode immersion depth is essential for good control of the process.

Electric furnace technology enables a wide range of process parameters to be used. For example, when low-iron concentrates are treated, a tin quality suitable for normal refining can be produced. The high-tin slags produced (up to 30% tin) are treated in a second stage to recover the tin. If the iron contents are much greater than 3%, the tin obtained has a high iron content (3–10%).

It is also possible to operate at ca. 1400 °C by using strongly reducing conditions. A tin-containing slag is then obtained together with hard head containing ca. 40% tin and 50% iron. The iron can be removed by smelting with ferrosilicon in a second pass, and a crude tin containing ca. 1% iron is obtained.

Great efforts have been made to overcome the disadvantage of batch operation of the electric furnace. For example, a continuously operated lengthened double chamber electric furnace has been reported in Russia. Each chamber has a hearth area of 1 m² and two electrodes. The reduced tin flows out of the first chamber over an air-cooled overflow, and

the tin is extracted from the high-tin slag in a second chamber [68]. The process is still at the pilot stage. The furnace capacity is reported to be less than 10 t/d.

Other Reduction Processes [1–3, 5, 30, 58, 60, 69]

All the processes described above have disadvantages, and many other methods and types of equipment have therefore been suggested for the reductive treatment of tin concentrates, but few of these proposals have led to an industrial plant.

One of the few methods tested at full scale is the top blown rotary converter developed in the United States and based on the “Kaldo” converter used in ferrous metallurgy. Oxygen is blown onto the top of charge as the converter rotates about its axis, which is set at an angle. The volume of waste gas is very low as there is no ballast nitrogen. The favorable heat transfer to the charge leads to a high reaction rate. Disadvantages include batch operation, a high rate of wear of the refractory lining, and the complexity of the system for controlling the oxygen lance.

After completion of the reduction process, the tin is tapped off. The tin in the remaining slag is vaporized as chloride by adding calcium chloride, and a discardable slag is thereby produced.

The tin chloride is scrubbed out of the waste gases and then precipitated as SnO₂ by adding CaO, regenerating CaCl₂.

The potential for transferring proven processes used in nonferrous metallurgy to tin metallurgy is discussed in detail in [69].

Developments over recent years suggest that no completely new processes for reducing tin concentrates have become established in the industry because of the high capital investment required and the hidden risks involved.

11.4.3.4 Slag Processing [1, 2, 5, 32, 38, 47, 62, 63, 70–79]

The slags produced during the reduction of high-tin concentrates can contain 5–10% of

the tin. This can increase to 20% in the case of low-grade and complex ores. One- or two-stage treatment of the slag is then necessary. It is in principle possible to use strongly reductive smelting (e.g., in a reverberatory or rotary furnace) or blowing processes to volatilize the zinc from the slag.

On reductive smelting, the tin and iron form an alloy, the so-called hard head, which is recycled to the primary tin production process. The secondary slag has such a low tin content that it can be removed from the process.

In the blowing process, the tin is converted into a flue dust, which is recycled to the primary smelting process. The slag, which usually has a high iron content, can be discarded.

Table 11.4: Tin and iron balance for two-stage smelting of a concentrate containing 73% Sn and 0.7% Fe based on 1000 kg concentrate treated.

	kg Sn	kg Fe
Smelting of concentrate		
Charge:		
1000 kg concentrate	730	7
95 kg hard head	38	42
220 kg coke/coal		2
40 kg flue dust	18	
11 kg recycled material	6	3
Total	792	54
Product:		
733 kg crude tin	730	5
200 kg primary slag	47	51
30 kg flue dust	15	1
Total	792	54
Smelting of slag		
Charge:		
200 kg primary slag	47	51
40 kg coke/coal		
Total	47	51
Product:		
100 kg secondary slag	1	8
95 kg hard head	38	42
10 kg flue dust	5	
2 kg Fe alloy		1
Total	44	51

Under production conditions, the intermediate products, e.g., the tin-containing secondary slag, the hard head, and the flue dusts, contain considerable quantities of tin. These are important for the economic operation of the process because of the amount of capital tied up if they are not immediately treated.

The tin and iron balances in the treatment of a concentrate with a very high tin content and a low iron content are shown in simplified form in Table 11.4.

The balance shows that the iron introduced into the concentrate smelting process with the concentrate and reducing agent (7 + 2 kg) must be removed from the slag smelting process in the secondary slag and iron-tin alloy (8 + 1 kg). Of the tin in the concentrate, 6% is in circulation in the primary slag (47 kg out of 730 kg).

However, the concentrates treated usually contain considerably more iron, so that a larger amount of primary slag and hard head are produced, and the amount of tin contained therein can rise to 20% of the raw material used.

In practical slag smelting, the SnO in silica-rich slags is mainly present as $2\text{SnO} \cdot \text{SiO}_2$, and the high activity of the SnO in silica- and lime-containing slags decreases with increasing FeO contents, so that in practice simultaneous reduction of tin and iron occurs. Theoretically, it is only possible to produce crude tin and low-tin slag if the FeO activities are extremely low. However, the processes would proceed at high temperatures with large additions of reducing carbon.

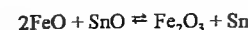
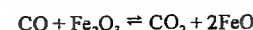
The binary Fe-Sn phase diagram shows a miscibility gap at $> 1100^\circ\text{C}$ between 20 and 50% Fe. On cooling to room temperature, separation of α -iron first takes place, followed by formation of FeSn and FeSn₂. At room temperature, the region of the composition of the hard head is always in the α -iron/FeSn two-phase region.

Wright has found by calculation of the distribution constant K at equilibrium

$$K = \left(\frac{\text{Fe}}{\text{Sn}} \right)_{\text{slag}} \cdot \left(\frac{\text{Sn}}{\text{Fe}} \right)_{\text{metal}}$$

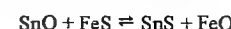
that the balance of the process is improved as the ratio in the first quotient increases, i.e., as the amount of iron removed in the slag increases. However, there must then be a higher iron concentration in the tin. If the tin in the

primary slag is present as $2\text{SnO} \cdot \text{SiO}_2$, the reaction mechanism is as follows:



Thus the reaction first occurs only at the surface of the carbon, and then via the iron oxides as intermediate phases. A high relative rate of reaction of carbon, slag, and reaction gas is therefore important for the reaction kinetics.

The reactions that occur in the detinning of slag are described in Section 11.4.3.2 (pyrometallurgical enrichment of low-grade concentrates), but here they start from SnO. As a matte phase must be present, the reaction will be:



As the slag is saturated with FeS, the amount of SnS formed is proportional to the activity of SnO in the slag, but indirectly proportional to the activity of FeO.

Reverberatory or electric furnaces are usually used in the reductive smelting process for the extraction of tin from primary reduction slags, though shaft kilns are occasionally used. The necessary intense reducing effect is achieved by adding 10–20% reduction carbon and by operating at temperatures up to 1500°C . In the electric furnace process, energy consumptions are 500–1000 kWh/t, and 1–10 kg electrode is consumed per tonne of slag. The reaction products, i.e., the final slag and the hard head alloy, are separated in settlers and then granulated in water.

As highly turbulent conditions are favorable to the process, reductive detinning can be carried out with a lance ("submerged combustion"), which produces a high reaction rate by agitation of the bath. Methane or natural gas

have been used as reducing gas, and experiments have also been carried out using hydrogen, carbon monoxide, and powdered solid fuels. Heat is produced by partial combustion of the injected gases and transferred to the molten slag. However, because SnO is volatile, 20% of the tin goes into airborne dust, a further undesired tin-containing reaction product in addition to the hard head.

An effective method of detinning primary tin reduction slags is by the blowing process, which can be carried out in reverberatory furnaces or true blowing furnaces. Gypsum or pyrite can be used as the sulfur source. The gypsum is first reduced to CaS, and then reacts with SnO to form SnS and CaO. If pyrite is used, impurities such as Pb, Zn, or As are introduced into the metallurgical process, adding to the difficulties of treating the tin-containing flue dusts. Blasting technology is also often used as the third stage of slag detinning. In the second stage, a thermal reduction, Sn contents of 2–5% and FeO contents of ca. 30% are obtained. The tin content of the molten slag in the furnace is reduced to ca. 0.5% by addition of sulfur sources. The addition of pyrite can be up to 400% of the theoretical amount calculated for the formation of SnS. Since smaller additions are possible in the case of acid slags, CaS is probably formed in basic slags. The treatment of primary slags in true blowing furnaces consists of blowing the pyrites into the molten slag. However, the process is discontinuous. The SnS vapor is oxidized in the furnace atmosphere, and recovered as SnO dust by filtration.

The slag blowing process can be carried out in furnaces of various designs, e.g., in a type of shaft kiln with a floor area of $0.5\text{--}6\text{ m}^2$ and a water-cooled shaft 7 m in height. The charge of primary slag can be 5–20 t. Cyclone and short drum kilns are also used. Process parameters, e.g., ratios of sulfur source to oxygen, fuel to atmospheric oxygen, and tin to sulfur must be carefully controlled to obtain optimum results.

Other proposed methods of detinning primary tin slags, such as vacuum-assisted volatilization of SnO (which has a considerably

lower vapor pressure than SnS), have not been used on an industrial scale [29].

11.5 Refining [1-3, 5, 32, 46, 47, 80-84]

The crude tin obtained by the reduction process is insufficiently pure for most applications.

Most national standards specify maximum contents of typical impurities. However, non-metallic impurities such as oxygen and sulfur and less common impurities such as noble metals are neglected, and the tin content is simply determined by subtracting the total amount of analytically determined impurities from 100.

The following three standard grades are accepted internationally: Sn 99.0%, Sn 99.75%, and Sn 99.9%.

There are some variations in these standards from country to country; the German standard is DIN 1704.

The level of impurities in the crude tin determines the extent of the refining operation. Treatment of very pure concentrates can give a tin content of up to 99.0% in the crude metal. The main impurity is iron (0.8%), the sum of all the other impurities being only 0.2%. In the case of low-grade and complex concentrates, the situation is very different, the tin content of the crude tin obtained sometimes being only 92%.

The impurities Fe, As, Sb, Cu, Ni, Pb, Bi, and the noble metals affect the amount of work involved in the refining process. The metals Zn, Cd, Mg, Si, Ca, Te, Se, and also sulfur and oxygen do not require special treatment, as they are present in the crude metal in only small concentrations, and are removed together with the other impurities during the various stages of purification. The phase diagrams for tin and its typical impurities lead to the following conclusions:

In the temperature range between 1000 and 1300 °C used in pyrometallurgical reduction, the impurities are completely soluble with the exception of Fe and Cr.

Only Sb, Cd, Bi, Zn, and Pb are significantly soluble in tin at room temperature. This is the basis for the removal of insoluble impurity elements by liquation. However, the liquation products have high tin contents, making costly recovery processes necessary.

In pyrometallurgical tin refining, the individual impurities are removed stepwise in batch processes. The use of the time-consuming operations is justified by their high selectivity.

Proposed continuous processes have not been operated on an industrial scale.

11.5.1 Pyrometallurgical Refining

11.5.1.1 Removal of Iron

The process for removing iron is based on the temperature dependence of the solubility of iron or Sn-Fe mixed crystals in tin. Accurate experiments have shown that the solubility of iron in tin at 250 °C is 0.0058% [81]. In industrial practice, even lower figures are achieved, which can only be explained by other impurities, such as Cu, As, or Sb, causing deviations from ideal solubility behavior. On cooling molten crude tin, α -Fe, γ -Fe, FeSn, and FeSn₂ precipitate successively. The density of the precipitated compounds is almost the same as that of the molten tin. In practice, "poling", i.e., passing steam or air into the melt, is used to coagulate the precipitated particles, which rise to the surface of the bath and are removed from the molten tin by filtration through graphite, slag wool, or a slab made of silica and limestone chippings. This should be carried out just above the melting point of tin, or in practice at a temperature not less than 260 °C. The process is sometimes carried out in two stages. Iron contents of 0.003-0.01% can be achieved.

As, Ni, Co, Cu, As, and Sb form intermetallic compounds with each other as well as with Fe, these impurities are also removed to some extent.

The treatment of the recovered intermetallic compounds is very complex, as these are in the form of a slurry with large amounts of ad-

hering molten tin. The iron content is only a few per cent, i.e., considerably less than that of the intermetallic compound FeSn₂.

The metal slurry is treated in small liquation furnaces. A controlled temperature increase over the range 230-300 °C enables pure tin to be removed, and a residue containing ca. 15% Fe suitable for use in the primary smelting stage to be obtained.

In high-capacity tin smelting works, high-temperature centrifuges are used. These enable a solid residue containing up to 25% Fe to be obtained [83].

11.5.1.2 Removal of Copper

After iron has been removed by liquation, the copper content is up to 0.01%. Elemental sulfur (2-5 kg/t) is stirred in at 250-300 °C, enabling copper contents as low as 0.001% to be attained. The resulting copper dross can be removed from the process after several stages of enrichment.

11.5.1.3 Removal of Arsenic

After removal of iron by liquation, the arsenic content is ca. 0.1%, significantly higher than permitted levels. For example, the commonly used Sn 99.75 grade should contain < 0.05% As according to DIN 1704.

Arsenic can be removed from the melts along with some Cu, Ni, and residual Fe by forming intermetallic compounds with aluminum. For this, the aluminum must be present as an ideal solution in the tin. For this reason, the melt must be heated to a temperature close to the melting point of aluminum before the aluminum is added. Special precautions are necessary, e.g., operation in a closed vessel so that the aluminum does not burn on the surface of the bath. The amount added must be approximately three times the stoichiometric amount. The use of Al-Sn master alloys enables the operation to be carried out at a lower temperature. Intense agitation if followed by a settling process with cooling to 350-400 °C, and the Al-As mixed crystals can then be re-

moved. Separation of the Al mixed crystals is assisted by poling.

With correct operation, As contents of < 0.02% can be achieved, i.e., below the permitted level for Sn 99.90%. This process enables Sb contents of 0.005%, Cu contents of 0.02%, and Ni contents of 0.005% to be attained, and any remaining Fe to be removed.

Any aluminum remaining in the molten tin can be removed by adding sodium, sodium hydroxide, chlorine, or steam, and residual sodium by adding sulfur.

The storage, transport, and treatment of the Al-As product presents problems. Contact with water must be avoided as this leads to the formation of highly toxic arsine and stibine. The material is stored in closed vessels and is converted into a safe product as soon as possible by oxidative roasting or by treating with alkali solution and collecting and burning the liberated arsine to form As₂O₃ and H₂O. The residues obtained both from the roasting and the leaching processes can be recycled to the process.

The large differences in vapor pressure between the impurities (arsenic, antimony, bismuth, and lead) and tin enable selective evaporation at reduced pressure to be used. However, numerous proposed processes have resulted in only two industrial applications.

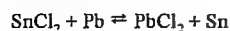
In a system tested in Russia, the impure tin flows from the top of a vertical reactor under a vacuum of 1 Pa into heated evaporating dishes. The evaporated impurities are collected in a separate chamber. Barometric valves are used to remove the purified tin and the condensate.

In the Bergsöe-Redlac system, a cylinder, cooled on the inside, rotates in a horizontal vacuum chamber above the melt, and the vaporized impurities are deposited on this in solid form. In the next stage of the process, they are scraped off and removed. The results of the vacuum distillation process depend on the reaction temperature and time. The high energy requirement for heating and for producing the vacuum, 400-700 kWh/t tin, is a disadvantage. Moreover, significant quantities of tin are vaporized. The use of selective evap-

oration of typical impurities in crude tin always involves a compromise between the purity and tin yield. Practical experiments are described in [85].

11.5.1.4 Removal of Lead

If the lead content is still not low enough after the first stages of the refining process, the lead can be converted into its dichloride by treatment with chlorine, tin dichloride, or tin tetrachloride:



The equilibrium is shifted to the right at low temperatures, so that the process must be carried out at a temperature only a little above the melting point of tin. The process also removes any remaining zinc and aluminum.

The best results are obtained by using two-stage operation, i.e., the product of the second stage, with a reduced lead content, is returned to the first stage. Precise control of the operation can lead to final lead contents of 0.008%.

11.5.1.5 Removal of Bismuth

In analogy to the thermal refining of lead, bismuth can be precipitated as an intermetallic compound by adding calcium or magnesium. The molar ratio Ca/Mg should be ca. 2 to obtain the best results [46]. A ternary compound is probably formed at this ratio. Under production conditions, scrap magnesium is used, as this is the most economic material.

Final bismuth contents of 0.06–0.003% have been reported for full-scale plant. In analogy to a technique used when removing arsenic from aluminum, the calcium and magnesium remaining in the tin can be converted to their chlorides and removed, e.g., by treatment with ammonium chloride.

11.5.2 Electrorefining

The theoretical conditions for the electrorefining of tin are favorable. The position of tin in the electrochemical series of the elements in aqueous solution show that Au, Ag, Cu, Bi, As, and Sb do not go into solution under elec-

trorefining conditions, but will appear in the anode slime. The elements Ni, Fe, Zn, and Al can be largely removed by a preliminary pyrometallurgical refining operation. Only lead lies close to tin in the electrochemical series. The high electrochemical equivalent weight of tin also favors the use of an electrometallurgical refining process. However, there are considerable problems in the practical realization of the process.

Simple and cheap electrolytes such as solutions of sulfate or chloride lead to spongy or needle-like deposits, and these effects are only slightly moderated by extremely large additions of colloidal materials. The process can only be operated at low current densities, leading to low process rates and inefficient utilization of energy (e.g., low current yields). Also, the presence of large amounts of expensive metal tied up in the process is undesirable economically.

These negative aspects mean that electrorefining is only worthwhile if the tin contains high concentrations of noble metals. Electrorefining can be carried out in acid or alkaline medium.

11.5.2.1 Electrorefining in Acid Medium

When sulfate electrolytes are used, additions of chloride, fluoride, crude cresol, glue, nicotine sulfide, α - and β -naphthol, diphenylamine, phenol, and/or cresolsulfonic acid are made. The sulfate ions cause the anodically dissolved lead to go into the anode slime in the form of lead sulfate. Also, sulfides such as nicotine sulfide can lead to the formation of lead sulfide, which is deposited in the anode slime. The organic sulfonic acids prevent the formation of basic tin salts on the anodes.

In spite of these precautions, the formation of coatings on the anode is the main problem in the electrolytic refining of tin in an acid medium. The main cause of coating formation is the lead content of the anodes, which must be removed mechanically when the bath voltage increases. The following operational data are quoted:

Anode mass:	100–200 kg
Anode thickness:	30 mm
Cell dimensions:	3.0–4.5 m long, 1.0–1.2 m wide, 1.0–1.5 m deep
Cell construction:	wooden cells with lead cladding or concrete
Cathode replacement:	after 6 d
Anode replacement:	after 10–12 d
Anode composition:	94–96% Sn, 0.01–0.03% Fe, 0.3–1.3% Pb, 0.1–0.6% Cu, 0.1–3.5% Bi, 0.02–0.35% As, 0.1–0.25% Sb, 100–300 g/t Ag, 0.3–0.7 g/t Au
Cathodes:	starter sheets of pure tin

The current yield is largely determined by the rate of removal of anode passivation. The energy consumption is 150–200 kWh/t tin. Because iron accumulates in the electrolyte, regeneration of the electrolyte is necessary.

11.5.2.2 Electrorefining in an Alkaline Medium

In alkaline medium, i.e., in NaOH or Na₂S electrolytes, less pure anodes (75% Sn) can be used than are used in an acid medium. A smooth deposit can be obtained without addition of colloids. However, current densities are very low, and the process must be carried out at 90 °C. Detailed information about the possibilities and limitations of electrorefining, deposition behavior, deposition mechanism, and effects of additives to the electrolyte, pH, and impurities are given in [4].

11.5.2.3 Other Methods of Electrorefining

Many attempts have been made to use molten salt electrorefining to overcome the disadvantages of electrorefining in aqueous solutions. The electrolyte was molten CaCl₂–KCl–NaCl. Various grades of crude tin were used. The electrodes consisted of graphite crucibles and graphite rods. The operating temperature was ca. 650 °C, and the current density 50–200 A/dm². Arsenic was effectively removed (reduced from 1.5% to 0.005%), and the antimony content was reduced from 0.32% to 0.01%. It proved impossible to scale up from pilot scale to full scale

operation, mainly because of problems in the control of the high-temperature process [77].

11.6 Recovery of Tin from Scrap Materials and Residues

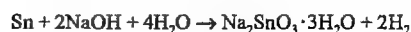
[1–3, 5, 11, 86, 87]

Scrap materials and residues which are produced during the processing of metals, to give semifinished and finished products are usually known as “new scrap”, while the returned old material from industry, trade, building construction, factories, and consumption is known as “old scrap”. The use of old and new scrap supplements primary production. It is collected by scrap merchants who work directly with the smelters. Also, in the neighborhood of metal smelting works there are often small scrap metal operations which sort, separate, refine and blend with primary metals to produce a primary metal that corresponds to the standard specification of an original metal [87].

The recovery of tin from tinplate is becoming increasingly difficult, as the change to electrolytic methods of tinning is leading to very thin coatings which sometimes diffuse into the steel sheet. The recycling of this material will continue to be a technically and economically difficult task. In principle, two processes are used today for recovering tin from tinplate: the alkaline electrolytic method and the alkaline chemical method.

In the alkaline electrolytic detinning of tinplate, baskets of cleaned scrap are immersed in hot 5–10% sodium hydroxide solution. The baskets form the anodes, and the tinned steel sheet forms the cathodes. The tin is deposited in the form of a sponge. As contact with atmospheric carbon dioxide cannot be prevented, sodium carbonate is formed, and the electrolyte bath must be frequently regenerated. The lacquer coating on the scrap tinplate is removed by adding solvents to the bath or by a special pretreatment process. The bath is operated at a temperature of 65–75 °C, a voltage of 1.5 V, and a cathode current density of 300 A/m².

In the alkaline chemical detinning of tinplate, the scrap material in perforated containers is immersed in sodium hydroxide solution. Hydrated sodium stannate is formed according to the equation



The hydrogen liberated must be reacted with an oxidizing agent; sodium nitrate is suitable. The dissolution process is accelerated by motion of the container in the liquor. The detinning time is 2–4 h, depending on the concentration and the temperature. If sodium nitrite is used instead of sodium nitrate, the tin goes into solution, the foreign metals, e.g., lead, iron, and antimony, can be precipitated, e.g., by hydrogen sulfide, and the tin can then be recovered by electrowinning.

Processing tin-containing alloys is easier than recovering tin from scrap tinplate. However, the tin content of many alloys has decreased over recent years, and alloys have in some cases been replaced by cheaper materials. Both these developments have tended to limit the potential for recovering secondary tin, and also explain why the amount of recovered tin in Europe has decreased from 15 800 t in 1980 to 13 300 t in 1990. In the United States, the amounts of recovered tin have remained almost constant at 16 900 t in 1980 and 17 100 t in 1990 [9].

The quantification of tin recovery from secondary raw materials is difficult because most of it is obtained from scrap alloy.

In addition to the tin concentrates treated in the primary smelting process, there are also other materials that must be treated, including the slags, oxidic flue dusts, ash, and sweepings containing very variable amounts of tin. Tin-containing processing scrap is also produced during casting, metal forming and cutting, tinning, and alloying. Considerable amounts of recycled scrap also come from the manufacture of cans, tinplate, tubes, foil, pure tin articles, and alloys such as solders, antifriction and bearing metals, type metal, etc.

In recycling it is essential to sort tin-containing materials into standard grades with ex-

act analytical specifications so that the metallurgical process can be optimized.

Short drum furnaces are suitable for processing oxidic materials, although shaft kilns and reverberatory furnaces are also used. The reduction is performed by coke/coal, with added sodium carbonate or fluorspar as flux. The process is operated in one or two stages, depending on the material. Scrap alloys containing high proportions of lead, antimony, or copper are remelted to form alloys. Scrap bab-bitt (bearing metal) contains zinc, which is either removed in the slag or selectively volatilized. Scrap solder alloys are refined like crude tin.

11.7 Analysis [88]

11.7.1 Analysis of Ores and Concentrates

Determination of Sn. In the determination of tin in ore concentrates, the choice of method depends on the presence or absence of typical impurities.

Tungsten-Free Ores and Concentrates. After fusion with sodium peroxide and dissolution in water, the solution obtained is acidified with hydrochloric acid and partially evaporated to drive off arsenic. The antimony is then precipitated with iron powder (cementation). The tin in the filtrate can then be "cemented" by adding aluminum powder, and determined by iodometric titration.

Tungsten-Containing Ores and Concentrates. The tungsten can be precipitated from the acidified solution by adding cinchonine. The excess of this reagent in the filtrate is decomposed by fuming with sulfuric acid. The solution is then taken up in hydrochloric acid and treated as in the determination of tin in tungsten-free ores.

Silicate-Containing Ores and Concentrates. The material is boiled to dryness with nitric acid, and the residue is then strongly heated, fumed with $\text{HF}/\text{H}_2\text{SO}_4$ and fused with sodium peroxide. The tin determination can

then be carried out as for tungsten-free materials.

Determination of Other Elements. The determination of tungsten is carried out by precipitating with cinchonine after the fusion stage. The precipitate is strongly heated (ca. 750 °C) to form WO_3 , and tungsten is then determined gravimetrically.

Arsenic is determined by distilling it out of the acidified solution of fused product and then carrying out a bromatometric titration on the distillate.

Antimony is determined by adding iron powder to the acidified fusion product to precipitate antimony sponge. This is dissolved in Br_2/HCl , and any arsenic still present is driven off by evaporating with HCl . The antimony is purified by reprecipitation, and determined by bromatometric titration.

For the determination of other elements such as cadmium, iron, nickel, copper, bismuth, lead, zinc, and the noble metals, it is best to remove zinc, arsenic, and antimony from the dissolved product of a sodium peroxide fusion (acidified with HCl) by evaporating with Br_2/HBr . The elements can be determined in the solution by atomic absorption spectrometry.

To determine sulfur, the sample is heated in a stream of oxygen, the SO_2 formed is collected in a dilute solution of H_2O_2 , and the H_2SO_4 formed is determined by titration. The sulfur content of the tin is calculated from this.

11.7.2 Analysis of Metallic Tin

The preferred methods of analysis of pure and commercial-grade tin are detailed in DIN 1704 [88].

Arsenic is determined by dissolving the metal in a strongly acidic solution of FeCl_3 . The AsCl_3 formed is distilled off, and can be determined photometrically by the molybdenum blue method.

Antimony is determined by dissolving the metal in concentrated sulfuric acid. After adding hydrochloric acid, the antimony is oxidized with cerium(IV) to antimony(V). This is then extracted with isopropyl ether and can be

determined photometrically as yellow potassium tetraiodoantimonate.

Lead is determined by dissolving the metal in a mixture of Br_2 , HBr , and HClO_4 , fuming this to volatilize the zinc, removing any Tl that might still be present by extraction with isopropyl ether, and determining the lead by polarography.

In the determination of copper, the initial dissolution is similar to that used in the determination of lead. The copper in the solution then is determined photometrically as the diethylthiocarbamate complex after extraction with CCl_4 .

The determination of zinc also requires a dissolution process similar to that for lead. The solution is acidified with hydrochloric acid, and heavy metals still present are precipitated as sulfides. The zinc in the filtrate obtained can be determined by polarography. Iron is determined by first carrying out the dissolution and precipitation of heavy metals as for zinc determination. The iron in the filtrate can be determined photometrically as the sulfosalicylic acid complex.

The determination of aluminum also requires dissolution and removal of heavy metals by precipitation of their sulfides as for iron determination. The aluminum in the filtrate can be determined photometrically as the eriochrome cyanine complex.

As well as the analytical methods recommended in DIN 1704, rapid and efficient methods such as atomic absorption spectrometry (AAS) and atomic emission spectrometry (ICP-AES) are also being used to an increasing extent [89]. These methods are specified in the German and international standards for the analysis of water, wastewater, and sewage sludge.

After dissolution of the tin in a mixture of Br_2 , HBr , and HClO_4 , the accompanying antimony, arsenic, bismuth, copper, iron, lead, aluminum, cadmium, and zinc can be determined with a high degree of accuracy in the presence of each other, without first separating them, by means of AAS and ICP-AES. In the determination of arsenic and antimony, other

dissolution processes must first be performed. The analysis of metallic tin and tin alloys is often carried out by spectral analysis with spark or arc excitation, and the analysis of tin slags and concentrates by X-ray fluorescence analysis.

Table 11.5: World production and consumption of tin (in 10^3 t).

Year	Mining output	Smelting output	Consumption
1980	235.5	243.6	221.4
1985	185.3	216.2	214.3
1990	210.7	225.6	232.7

Table 11.6: Mining output and consumption of tin in various countries in 1990 [9].

Country	Mining output		Consumption	
	in 10^3 t	as %	in 10^3 t	as %
Brazil	39.1	18.6	6.1	2.6
Indonesia	37.1	15.1	1.4	0.6
Malaysia	28.5	14.3	3.3	1.4
Bolivia	17.3	8.2	0.4	0.2
China	35.8	17.0	18.0	7.7
Russia	13.0	6.1	20.0	8.5
United States	0.1	0.04	37.3	16.0
Japan			33.8	14.5
Germany			19.3	8.2
United Kingdom	3.4	1.6	10.4	4.3

11.8 Economic Aspects [2, 9, 11]

There have been no large variations in the amounts of tin mined, smelted, and consumed in recent years. Figures for the years 1980–1990 are given in Table 11.5.

Even in 1938, smelting production amounted to 171 200 t [3], and this had increased by only 66 500 t or 38.8% in 1990. This is an average increase of 9.75% per annum.

Typically in the production and consumption of tin, the production processes of mining and smelting are geographically remote from the places where the metal is consumed.

The main producers, i.e., Brazil, Indonesia, Malaysia, Bolivia, and to some extent China, consume very little tin themselves (see Table 11.6). On the other hand, the United States, Japan, Germany, and the United Kingdom produce little or no primary tin themselves and are the main tin consumers. In the CIS, pro-

duction and consumption are approximately equal.

The continuous fall in the price of tin (> 30 000 DM/t in 1985, ca. 10 000 DM/t in 1990) has led to many casualties worldwide. The worst effects have been in Malaysia, where over 80 suppliers have been closed down. In 1980, Malaysia was the main producer of tin, with a mine output of 61 000 t. This fell to 28 500 t in 1990, and Malaysia now produces less tin than Brazil, China, or Indonesia. Even the well-known tin smelter Capper Pass in the United Kingdom has ceased production, as have the tin mines in the Altenberg region of Saxony.

11.9 Alloys and Coatings [1, 2, 11]

Tin is one of the most important constituents of low-melting nonferrous alloys. The following important properties of the metal are exploited

- Low melting point
- Low hardness
- Good wetting properties
- Effective incorporation of foreign particles
- Good compatibility with foodstuffs

Tin utensils have been produced for over 5000 years, and well-preserved examples exist from the various epochs.

Tin utensils are always made of tin alloys, as the pure metal is too soft. The most important alloying elements are antimony, copper, and lead. The tin is usually melted first, and it then readily forms alloys with pure metals, which have good solubility properties. To minimize burning, especially of antimony, master alloys are usually used.

Solders. Most solders are based on the tin lead binary system, which has a eutectic at ca. 63% tin and 183 °C. The solid solubility of 1–2% lead in tin and 13% tin in lead is not relevant to production conditions.

Although the copper–tin alloys are some of the oldest materials used by humans, their development is not yet exhausted even today.

The most important development aims are improvement of mechanical properties and corrosion resistance, and reduction of the tin content.

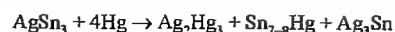
Sintering Metallurgy of Bronzes. An interesting new use for tin is as an addition in powder form when sintering bronze. Especially when this is for use as a bearing metal, economic advantages are obtained by the addition of 4% tin to the copper powder with or without lead addition.

Low-melting alloys are of great importance in several technical applications. Their melting points usually lie significantly below 150 °C. Bismuth is always an essential alloy constituent.

Their most important application areas are in mold making, safety systems for the prevention of fire and overheating, and stepwise soldering.

Amalgams. Tin has been used for dental fillings since the Middle Ages, and amalgams since the 1800s. Subsequent developments have led to the silver–tin amalgams used today. A typical amalgam has the following composition: 52% Hg, 33% Ag, 12.5% Sn, 2% Cu, 0.5% Zn.

When the mixture of metals is ground together, the following hardening reaction takes place:



The metallographic structure of a dental amalgam consists of islands of solid undissolved particles of alloy (Ag_3Sn) in a soft matrix of silver and tin amalgams.

11.10 Compounds

Consumption of inorganic tin compounds is lower than that of organic tin compounds, but they are often the starting materials used to produce the organic tin compounds.

In minerals, tin is nearly always tetravalent and bonded to oxygen or sulfur. The only exception is herzenbergite, SnS , in which it is divalent.

In industry, tin(II) and tin(IV) compounds are produced from metallic tin. Many tin(II) compounds which are sufficiently stable for practical purposes have a strong tendency to change into tin(IV) compounds and are therefore strongly reducing. For example, SnCl_2 precipitates gold and silver in metallic form from their salt solutions.

The salts in both valency states hydrolyze in aqueous solution to form insoluble salts. In alkaline media, stannites (divalent) and stannates (tetravalent) are formed.

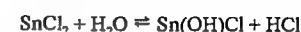
11.10.1 Tin(II) Compounds

Tin(II) chloride, SnCl_2 , is the most important inorganic tin(II) compound. It is produced on an industrial scale by reducing tin(IV) chloride with molten tin, or by direct chlorination of tin.

Solutions of tin(II) chloride are obtained by dissolving metallic tin in hydrochloric acid, or by reducing a solution of SnCl_4 with metallic tin.

The anhydrous substance is white, has a greasy luster, and dissolves readily in water, alcohol, ethyl acetate, acetone, and ether. The clear, nondeliquescent, monoclinic dihydrate $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, crystallizes from aqueous solution and is the commercial product.

On dilution, the aqueous solution becomes cloudy as hydrolysis causes precipitation of the basic salt:



The cloudiness can be prevented by small additions of hydrochloric acid, tartaric acid, or ammonium chloride. Because of its strong tendency to hydrolyze, the dihydrate can only be dehydrated over concentrated sulfuric acid or by heating in a stream of hydrogen chloride.

Tin(II) chloride is an important industrial reducing agent, being used to reduce aromatic nitro compounds to amines, aliphatic nitro compounds to oximes and hydroxylamines, and nitriles to aldehydes.

Tin electroplating can be carried out in a fused eutectic salt mixture of 20% SnCl_2 and 80% KCl at 200–400 °C [90, 91].

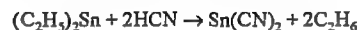
Tin(II) Oxide Hydrate and Tin(II) Oxide. If aqueous solutions of SnCl_2 or other tin(II) salts are reacted with alkali metal carbonate or ammonia, an amorphous white precipitate of tin(II) oxide hydrate, $5\text{SnO} \cdot 2\text{H}_2\text{O}$, is obtained [92]. $\text{Sn}(\text{OH})_2$ does not exist. Tin(II) oxide hydrate is amphoteric. Dehydration in a stream of carbon dioxide gives tin(II) oxide. Tin(II) oxide hydrate and tin(II) oxide are starting materials for the production of other tin(II) compounds.

Other Tin(II) Compounds. Tin(II) fluoride, SnF_2 , is formed from tin(II) oxide hydrate and hydrofluoric acid, and is added to toothpastes as an anticaries agent.

Tin(II) fluoroborate hydrate, $\text{Sn}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$, is formed by dissolving the oxide hydrate or the oxide in aqueous fluoroboric acid. Sulfuric acid reacts with the oxide hydrate or the oxide to form tin(II) sulfate. Both tin(II) sulfate and tin(II) fluoroborate are important in the production of metallic tin coatings by electroplating.

Tin(II) bromide, SnBr_2 , and *tin(II) iodide*, SnI_2 , are produced by reacting metallic tin with the appropriate hydrogen halide.

Tin(II) cyanide, which is produced from bis(cyclopentadienyl)tin(II) and hydrogen cyanide, is the only known compound of tin with inorganic carbon:



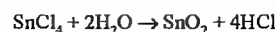
The tin(II) salt of ethylhexanoic acid is an effective catalyst in polyurethane production.

11.10.2 Tin(IV) Compounds

Tin(IV) Hydride. The toxic, colorless, flammable gas, tin(IV) hydride, is formed by the reduction of tin(IV) chloride by LiAlH_4 in diethyl ether at -30°C . It is stable for several days at room temperature, and decomposes into its elements at 150°C in the absence of air, forming a tin mirror.

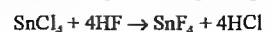
Tin(IV) Halides and Halostannates(IV). Anhydrous tin(IV) chloride is a colorless liquid which fumes strongly in air. It is a good solvent for sulfur, phosphorus, and iodine, and is miscible in all proportions with carbon di-

sulfide, alcohol, benzene, and other organic solvents. It hydrolyzes in water, evolving much heat and forming colloidal tin(IV) oxide and hydrochloric acid:



In moist air, the pentahydrate, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, is formed, the so-called butter of tin, a white deliquescent crystalline mass with a melting point of 60°C . In industry, SnCl_4 is produced by the reaction of chlorine with tin. The anhydrous product is obtained if the metal is covered with SnCl_4 . Anhydrous tin(IV) chloride is an important starting material for the production of organic tin compounds.

Tin(IV) bromide, SnBr_4 , and tin(IV) iodide, SnI_4 , are also obtained by the reaction of metallic tin with the halogens. Tin(IV) fluoride is produced by the reaction of tin(IV) chloride with anhydrous hydrogen fluoride:



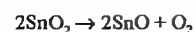
Tin(IV) halides react readily with metal halides to form the halostannates(IV), the coordination number of the tin increasing from four to six. The reaction proceeds as follows (X = halogen):



One of the best known compounds of this type is ammonium hexachlorostannate, $(\text{NH}_4)_2\text{SnCl}_6$, the so-called pink salt.

Hexachlorostannic acid, $\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$, is formed by passing HCl into a concentrated solution of SnCl_4 .

Tin(IV) Oxide, Tin(IV) Oxide Hydrate, and Stannates(IV). Tin(IV) oxide decomposes above 1500°C without melting to form tin(II) oxide:



Pure tin(IV) oxide can be obtained by the combustion of powdered tin or sprayed molten tin in a hot stream of air. It is insoluble in acids and alkalis. Specially prepared tin(IV) oxide has many uses, total world consumption of this material being > 4000 t/a. It is used in combination with other pigments to produce ceramic colorants. It has a rutile structure, and hence can absorb the colored ions of transition

metals. The products obtained form the basis of ceramic colors, and include tin vanadium yellow, tin antimony gray, and chrome tin pink. The thermal stability of the tin colors enables them to be used both in and under the glaze.

Electrodes made of SnO_2 are used in the production of lead glass [93]. They are resistant to corrosion by molten glass, and have good electrical conductivity when hot.

Coatings of tin(IV) oxide treated with indium oxide ($< 100 \mu\text{m}$ thick) give good transparency properties to aircraft window systems, increase their strength, and give protection from icing.

If tin(IV) oxide is reacted with a solution of alkali, or a solution of stannate is reacted with acid, a white, gel-like precipitate of tin(IV) oxide hydrates is formed which are very soluble in alkalis and acids. This precipitate was formerly known as " α -stannic acid", and the aged product, which is sparingly soluble, as " β -stannic acid" (metastannic acid). Today, this product is regarded as tin(IV) oxide hydrate with the formula $\text{SnO}_2 \cdot n\text{H}_2\text{O}$, where n decreases with aging.

The reaction of powdered or granulated tin with concentrated nitric acid leads to the formation of the reactive β -tin(IV) oxide hydrate. This can be used as a catalyst for aromatics.

The β -tin oxide hydrate gels precipitated from SnCl_4 by ammonia and then dried are stable towards nuclear radiation, and can be used in chromatographic columns for separating radioactive isotopes [94].

Fusion of tin(IV) oxide with alkali metal hydroxides leads to formation of alkali metal hexahydroxystannates according to the following reaction scheme (M = alkali metal):



The sodium and potassium complexes are used as alkaline electrolytes in electrolytic tin plating.

Tin(IV) sulfide, SnS_2 , is formed as golden yellow flakes with a hexagonal crystal structure by passing hydrogen sulfide through a weakly acidic solution of a tin(IV) salt. On

heating, the crystals become dark red to almost black, reverting to yellow on cooling.

The tin disulfide known as "mosaic gold" is produced industrially by heating tin amalgam with sulfur and ammonium chloride. It is used for gilding picture frames, and in painting to produce deep yellow to bronze color shades.

11.11 Toxicology

Metallic tin is generally considered to be nontoxic. As early as the Middle Ages, it was used in the form of plates, jugs, and drinking vessels. Even large amounts of tin salts in the digestive system cause negligible harm. Apparently, tin can migrate only very slowly through the intestinal walls into the blood. Orally ingested tin is poorly resorbed by animals and humans. The half-life in the kidneys and liver is 10–20 d, and in the bones 40–100 d. Cases of poisoning are almost unknown. Massive inhalation of tin or tin oxide dust by exposed industrial workers can lead to irritation of the respiratory tract. In extreme cases, metal fume fever with similar symptoms to those of "zinc fever" or "brass fever" also occurs. As the peroral ingestion of tin and its inorganic compounds is comparatively harmless because of the relatively low resorption, the limit value for the prevention of sickness and diarrhea for fruit preserves is ca. 250–500 mg/kg, and for fruit juices 500–1000 mg/kg. In current industrial practice, the tin cans are additionally lacquered, and the tin concentrations in preserved fruit and vegetables are < 250 ppm. The MAK value, calculated as tin and measured in total dust, has been 2 mg/m^3 for many years [95, 96].

Hydrochloric acid formed by the hydrolysis of tin chloride can cause acid burns. Tin hydride is very toxic, having a similar effect on the human organism to arsine [97].

Organotin compounds are very toxic; the MAK value is 0.1 mg/m^3 [96]. These compounds can differ widely in their effects, and can also be slowly converted to other compounds in the organism, so that toxic symptoms can change during the induction time.

The toxicity of alkyl and aryl tin compounds decreases in the series: trialkyl > dialkyl > tetraalkyl > monoalkyl compounds. Whereas tributyl- and triphenyltin compounds are almost as toxic as HCN, the monoalkyl compounds have a toxicity similar to that of the inorganic tin compounds.

The resorption of tin alkyl and tin aryl compounds can have harmful effects on the CNS, such as edema of the brain and spinal cord and damage to the respiratory center. The volatile organotin compounds cause persistent headaches, epileptiform convulsions, narcosis, and respiratory paralysis.

Dibutyltin dichloride, tributyltin chloride, and analogous alkyl tin halides, after a latent period, cause irritating and burning of the skin and especially the mucous membranes, and are intensely sternutatory and lachrymatory [98, 99].

In cases of poisoning by organotin compounds, long-term observation of the functioning of the liver and CNS is necessary.

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12 Nickel

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12.1 Introduction

Nickel is a silver white metal with typical metallic properties. It occurs in the periodic table in the first triad of Group VIII (IUPAC Group 10), after iron and cobalt, to which it is closely related. The electronic configuration of nickel is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$.

Nickel occurs naturally as a mixture of five stable isotopes of mass number 58 (67.84%), 60 (26.23%), 61 (1.19%), 62 (3.66%), and 64 (1.08%). So far even artificial radioactive isotopes have been identified with mass numbers of 56, 57, 59, 63, 65, 66, and 67.

The great importance of nickel lies in its ability, when alloyed with other elements, to increase a metal's strength, toughness, and corrosion resistance over a wide temperature range. Nickel is essential to the iron and steel industry, and nickel-containing alloys have played a key role in the development of materials for the aerospace industry. World production of nickel increased from 20×10^3 t/a in 1920 to 750×10^3 t/a in 1976 at an average annual rate of increase of 3%. However, no significant increase in either consumption or production occurred between 1976 and 1986, with world nickel consumption falling as low as 650 000 t/a in 1981 and 1982. The known world reserves of nickel are more than adequate to maintain this level of production for many years.

12.1.1 History [1-4]

It is believed that the word "Nickel" or "Kupfer Nickel" is derived from a derogatory term applied by medieval miners in Saxony to a mineral which they mistakenly believed to be a copper ore, but from which they could extract no copper. It was in fact the nickel arsenide ore niccolite (NiAs). The Saxon miners not unnaturally assumed that evil spirits, or "Old Nick" himself, were responsible for their problems.

Nickel was first isolated by the Swedish mineralogist AXEL CRONSTEDT in 1751, when studying a gersdorffite (NiAsS) ore from Los in Sweden. Nickel's status as an independent

element was proved in 1775 by TORBERN BERGMAN and coworkers, but it was not until 1804 that JEREMIAS RICHTER produced a relatively pure sample of the metal and described its essential properties.

Nickel-containing alloys were in use long before CRONSTEDT's discovery. For centuries the Chinese had been making "pai thung" or "white copper" (40% Cu, 32% Ni, 25% Zn, and 3% Fe) which resembled silver in appearance. This material appeared in Europe in small quantities in the late 1700s. Since it costs only one quarter the price of silver, the alloy had obvious commercial potential as a silver substitute. By the 1830s, copper-nickel-zinc alloys, by then known as German Silver and later as nickel-silver, were being produced commercially in both Germany and England in significant amounts. In addition to its silver color, this alloy was easy to cast and fabricate, was resistant to tarnishing, and was economical to produce. The next significant development occurred in 1857 when the United States issued a cupronickel coin containing 12% nickel; other countries soon followed suit.

In the mid-1800s nickel was produced in small quantities from sulfide ores mined in Germany, Norway, Sweden, and Russia. Although refined metallic nickel was first produced in Germany in 1838, world production of nickel remained below 1000 t/a until 1876.

The demand for nickel increased abruptly in 1870-1880 when PARKES, MARBEAU, and RILEY demonstrated its use in alloy steels, as FLEITMANN succeeded in making malleable nickel, and as electrolytic nickel plating was successfully developed. The first nickel-steel armor plate was made in France in 1885 and soon afterwards in Italy, England, and the United States. In the early 1890s the adoption of nickel steels by the world's navies led to a steep rise in the demand for nickel.

In 1863, PIERRE GARNIER discovered the nickel oxide ores of New Caledonia, and from 1875 this French island became the world's main producer of nickel, which position it retained until displaced by Canada in 1905. Mining of the sulfide ores of the Sudbury Ba-

sin in Ontario, Canada, started in 1886, and these ore bodies were to remain the most important source of the world's nickel supply for most of the twentieth century. Even in 1950 the Sudbury area still supplied 95% of the nickel for the Western world. Since then Canada's preeminent position has been largely eroded, and by 1980 nickel was being mined, smelted, and refined in more than 20 countries.

Up to the end of World War I nickel was used almost exclusively for military purposes, but intensive research, between the world wars, into potential industrial uses soon led to a variety of new applications. In the 1990s there are thousands of nickel alloys in use with nickel contents ranging from 99% in wrought nickel to as little as 1% as hardening additives for various alloys.

12.1.2 Physical Properties

The physical properties of nickel [9-11] depend largely on its purity, on the physical state of the metal, and on its previous treatment. The wrought metal is highly malleable, moderately strong, tough, ductile, and highly resistant to corrosion in many media. Its good strength and ductility persist to subzero temperatures. Some important physical properties of nickel are as follows:

<i>mp</i>	1455 °C (1728 K)
<i>bp</i>	2730 °C (3003 K)
Relative density (25 °C)	8.9
Volume increase on melting	4.5%
Heat of fusion (<i>mp</i>)	302 J/g

Heat of sublimation (25 °C)	7317 J/g
Heat of vaporization (T_{crit})	6375 J/g
Standard entropy	29.81 J/K
Thermal conductivity (0-100 °C)	88.5 W m ⁻¹ K ⁻¹
Heat capacity (0-100 °C)	0.452 J g ⁻¹ K ⁻¹
Electrical resistivity (20 °C)	6.9 μΩ/cm
Temperature coefficient of electrical resistivity (0-100 °C)	6.8×10^{-3} K ⁻¹
Thermal expansion coefficient (0-100 °C)	13.3×10^{-6} K ⁻¹
Modulus of elasticity	199.5 GPa _p
Brinell hardness	85

The density of molten nickel in g/cm³ is given by

$$\rho = \rho_0 - 1.16 \times 10^{-3} (t - t_0)$$

where

$$\rho_0 = 7.905, \quad t_0 = 1455;$$

the surface tension in mN/m, by

$$\sigma = \sigma_0 - 0.38 (t - t_0)$$

where

$$\sigma_0 = 1778, \quad t_0 = 1455;$$

and the viscosity in mPa·s, by

$$\eta = \eta_0 e^{E/RT}$$

where

$$\eta_0 = 0.1663, \quad E = 855 \text{ J/g}$$

Some mechanical properties of nickel are listed in Table 12.1.

Nickel normally forms a face-centered cubic crystal lattice, although a hexagonal modification is known, which changes to the cubic form at 250 °C. Cubic nickel is ferromagnetic below its Curie point of 357 °C, although less so than iron. The hexagonal form of nickel is not ferromagnetic.

Table 12.1: Mechanical properties of nickel (nominally 99.0% Ni).

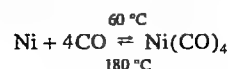
Property	Pretreatment							
	Tempered			Hot-rolled				
Temperature, °C	-200	-75	20	20	200	400	600	800
0.2% proof stress, MPa	230	170	160	170	150	140	110	
Tensile strength, MPa	710	560	500	490	540	540	250	170
Elongation, %	54	58	48	50	50	50	60	60
Impact value (Charpy)	230	230	230					

12.1.3 Chemical Properties

In its chemical properties [12] nickel resembles iron and cobalt, as well as copper. The +2 oxidation state is much the most important in nickel chemistry, although the +3 and +4 oxidation states are also known. The oxidation of nickel(II) salt solutions with chlorine, bromine, or persulfate in aqueous alkaline solution produces the insoluble nickel(III) oxide, β -NiO(OH). The nickel(IV) oxide $\text{NiO}_2 \cdot n\text{H}_2\text{O}$ is prepared by persulfate oxidation of nickel(II) hydroxide. In contrast to cobalt and iron, nickel is normally only stable in aqueous solution in the +2 oxidation state.

Nickel(II) ions form complexes very readily. The maximum coordination number is six. The green color of most hydrated nickel(II) salts and their aqueous solutions is due to the octahedral $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ cation. The strong tendency of the nickel(II) ion to form complexes with ammonia, for example $\text{Ni}(\text{NH}_3)_6^{2+}$, or $\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4^{2+}$, is utilized in a number of extraction processes.

The most unusual property of nickel is its ability to react directly with carbon monoxide to form a binary carbonyl complex. When carbon monoxide reacts with metallic nickel at 60 °C it forms the volatile nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$. This reaction is reversible, with the carbonyl compound decomposing to carbon monoxide and nickel at higher temperatures (180 °C).



This reaction is the basis for the vapometallurgical refining of nickel. No other metal forms similar carbonyl compounds under such mild conditions at atmospheric pressure.

At moderate temperatures nickel has a high corrosion resistance against air, seawater, and nonoxidizing acids. Nickel is fairly electropositive with a standard electrode potential of -0.25 V, which is similar to cobalt (-0.28 V).



An outstanding property of nickel is its corrosion resistance to alkalis. The metal is therefore frequently used in the production and

handling of caustic soda. In contrast, nickel is attacked by aqueous ammonia solutions.

Nickel absorbs hydrogen, especially when finely divided; hydrogen absorption increases with increasing temperature. Defined hydride compounds have not been characterized. Nitrogen is not absorbed by nickel nor does it combine directly with it, although there is evidence for a nitride Ni_3N .

12.2 Occurrence

Nickel ranks twenty-fourth in the order of abundance of elements in the earth's crust with an estimated concentration of 0.008%. Although nickel is more abundant than copper, zinc, and lead there are relatively few nickel ore bodies of commercial significance.

The economically important ores can be divided into two types, sulfide and oxide (or silicate). Nickel does not occur as native metal. World reserves of nickel are currently (1988) estimated at about 50×10^6 t by the U.S. Bureau of Mines. This estimate includes only ores which are economically recoverable at prevailing metal prices. Identified world resources in deposits containing 1% Ni or more amount to over 130×10^6 t of nickel. About 80% of the nickel in these resources is in laterite ore bodies, with only 20% in sulfide deposits. The distribution of high-grade nickel reserves are detailed by country in Table 12.2, together with the corresponding 1988 mine production rates [13].

Nickel-containing manganese nodules, which occur in vast quantities on the seabed at depths between 3500 and 4000 m, typically contain 0.5–1.5% Ni. While not currently economically viable as a source of nickel, these deposits will undoubtedly become an increasingly important nickel resource in the future.

The United States has significant quantities of low-grade nickel resources such as the laterite ores of Oregon and northern California. However, none of these ores was considered as an economic nickel reserve by the Bureau of Mines at 1988 metal prices, and

consequently they are omitted from Table 12.2.

Table 12.2: World reserves of nickel [13].

Country	Reserves, 10^3 t	1988 Mine production, 10^3 t
Albania	180	10
Australia	1 270	74
Botswana	354	16
Brazil	666	15
Canada	8 130	190
China	726	25
Colombia	558	21
Cuba	18 140	34
Dominican Republic	517	23
Finland	80	11
Greece	454	12
Indonesia	3 200	58
New Caledonia	4 535	56
Philippines	408	8
South Africa	2 540	34
Former Soviet Union	6 620	186
Yugoslavia	158	4
Zimbabwe	77	11
World total	48 980	788

Table 12.3: Principal nickel minerals [1].

Mineral	Ideal formula	Nickel content, %
Sulfides		
Pentlandite	$(\text{Ni}, \text{Fe})_9\text{S}_8$	34.22 ^a
Millerite	NiS	64.67
Hawleyite	Ni_3S_2	73.30
Polydymite	Ni_3S_4	57.86
Siegenite	$(\text{Co}, \text{Ni})_3\text{S}_4$	28.89
Violarite	Ni_2FeS_4	38.94
Arsenides		
Niccolite	NiAs	43.92
Rammelsbergite	NiAs_2	28.15
Gersdorffite	NiAsS	35.42
Antimonides		
Breithauptite	NiSb	32.53
Silicates and oxides		
Garnierite	$(\text{Ni}, \text{Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	≤ 47
Nickeliferous limonite	$(\text{Fe}, \text{Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$	low

12.2.1 Minerals

The most important nickel-containing minerals occurring in nickel deposits are listed in Table 12.3, together with their chemical compositions [1]. Some are relatively uncommon, and only pentlandite, garnierite, and nickeliferous limonite are of economic significance. The term garnierite is commonly used as a ge-

neric name for a series of mixed nickeliferous silicates with a wide range of nickel contents, and can include colloidal mixtures of silica and nickel hydroxide. Nickeliferous limonite is the term used to describe poorly crystalline nickel-bearing ferric oxides of which the main constituent is goethite (α -FeO·OH).

Pyrrhotite ($\text{Fe}_{n-1}\text{S}_n$) is not included in the list of nickel minerals because it is an iron sulfide, and nickel is not essential to its composition. In pyrrhotites from different ore bodies the composition varies from FeS to Fe_7S_8 . Small amounts of nickel may substitute for the iron, making some pyrrhotite nickeliferous, independently of any particles of pentlandite they may contain.

12.2.2 Sulfide Ores

Sulfide nickel ores consist principally of nickeliferous pyrrhotite (Fe_7S_8), pentlandite ($(\text{Ni}, \text{Fe})_9\text{S}_8$), and chalcopyrite (CuFeS_2). Other minerals which occur in small but significant amounts include magnetite (Fe_3O_4), ilmenite (FeTiO_3), pyrite (FeS_2), cubanite (CuFe_2S_3), and violarite (Ni_2FeS_4). Sulfide ores typically grade 0.4–2.0% nickel, 0.2–2.0% copper, 10–30% iron, and 5–20% sulfur. The balance consists of silica, magnesia, alumina, and calcium oxide.

Pentlandite, the commonest of the sulfide minerals, probably accounts for 60% of world nickel production. Nickeliferous pyrrhotite is normally the most abundant phase in a nickel ore. It contains nickel in solid solution (0.2–0.5% Ni) in addition to very finely divided pentlandite inclusions. Chalcopyrite is the most important copper mineral, although cubanite is often present in lesser amounts.

Although the major minerals are the same in all large sulfide ore bodies, the relative amounts of pyrrhotite, pentlandite, and chalcopyrite vary widely. The relative amounts of the three minerals largely determine the choice of processing route.

In addition to nickel production, a large number of valuable by-products can be recovered from sulfide ores, including copper, cobalt, the platinum group metals, gold, silver,

selenium, tellurium, sulfur, and iron. Cobalt occurs principally in solid solution in pentlandite, at concentrations ranging from 1 to 5% of the nickel content. Discrete particles of gold, silver, and platinum group metals are very rare, and these metals are normally found in solid solution in the sulfide phases. The treatment processes are normally designed to yield optimum overall recovery of metal values.

Major sulfide ore bodies occur in Canada, the former Soviet Union, the Republic of South Africa, Australia, Zimbabwe, and Finland.

12.2.3 Oxide Ores

The oxidic ores of nickel are formed by a chemical concentration process that occurs as a result of the lateritic weathering of peridotite rock. Peridotite consists mainly of olivine, a

magnesium iron silicate containing up to 0.3% nickel. In many rocks the peridotite has been altered to serpentine, a hydrated magnesium silicate, prior to exposure to weathering. Olivine and serpentine are decomposed by groundwater containing carbon dioxide to form soluble magnesium, iron, and nickel, and colloidal silica. The iron rapidly oxidizes in contact with air and precipitates by hydrolysis to form goethite and hematite, which remain near the surface of the deposit. The dissolved nickel and magnesium, and the colloidal silica, percolate downwards in the laterite deposit, remaining in solution so long as the solution is acidic. When the solution is neutralized by reaction with rock and soil, nickel, silica, and some of the magnesium precipitate as hydrated silicates. This process is illustrated in Figure 12.1 [14].

Idealized laterite	Approximate analysis, %					Extractive procedure
	Ni	Co	Fe	Cr ₂ O ₃	MgO	
Hematitic cap	<0.8	<0.1	>50	>1	<0.5	Overburden to stockpile
Nickeliferous limonite	0.8 to 1.5	0.1 to 0.2	40 to 50	2 to 5	0.5 to 5	Hydrometallurgy
Altered peridotite	1.5 to 1.8	0.02 to 0.1	25 to 40	1 to 2	5 to 15	Hydrometallurgy or pyrometallurgy
Unaltered peridotite	0.25 to 0.02	0.01 to 0.02	5 to 25	0.2 to 1	35 to 45	Pyrometallurgy
						Left in situ

Figure 12.1: Typical section through a laterite deposit.

Complete separation of iron and nickel into distinct zones is never achieved. Some or even most of the nickel may in fact remain in the upper layer, which is thus enriched in iron and nickel, but depleted in magnesium and silica. Such material, consisting mainly of ferric oxide minerals, is described as limonitic. This type of ore is typically relatively rich in cobalt and chromium. By contrast, in the silicate minerals, the separation of iron and nickel is more complete, and the nickel is present in silicate minerals with a high magnesia content. Both types of material are almost always found in a laterite deposit, but in widely differing proportions.

The differences between limonitic and silicate minerals influence the methods by which they are treated for nickel recovery (Figure 12.1). The silicates, which are chemically and mineralogically heterogeneous and require a very flexible processing method, are normally treated by pyrometallurgical processes. The limonites on the other hand are relatively homogeneous in composition and mineralogy and are well suited to hydrometallurgical treatment.

The type of weathering which dissolves silica and metallic elements from rock to produce limonitic and silicate nickel ores occurs most frequently in tropical climates with high rainfall, and with decomposing vegetable matter to provide organic acids and carbon dioxide in the groundwater. Oxide nickel mineral deposits are currently exploited in Australia, Brazil, Cuba, the Dominican Republic, Greece, Indonesia, the Philippines, New Caledonia, Yugoslavia, the United States, and the former Soviet Union. The laterite deposits in Oregon and California were formed when the climate was subtropical in past geologic epochs.

12.2.4 Economic Trends

Although 80% of the world's known nickel resources on land are in oxide ore bodies, only 40% of nickel production comes from this source. The greater part of the nickel produced is recovered from sulfide ores. This situation

has arisen from the influence of political, geographic, technical, and economic factors. Sulfide ore deposits lie mostly in politically stable countries and close to the major nickel markets. The nickel content of sulfide ores can be concentrated relatively easily and cheaply by physical methods, while oxide ores must be treated in bulk. The potential for recovering the more numerous and valuable by-products also favors the exploitation of sulfide ore. However, the grades of sulfide ores are continually declining as the richer ores are consumed, and the cost of underground mining, particularly labor costs, is continually increasing. Inevitably therefore, oxide ore bodies, which are all relatively uniform in grade and can be surface mined, must in future support a larger share of nickel production.

Unfortunately, the production of nickel from oxide ores by the established processes consumes two to three times as much energy as the processing of sulfide ores. Nickel oxide ore treatment is therefore very sensitive to fuel oil and electrical power costs. A major expansion in the exploitation of oxide ores occurred in the decade prior to 1973 when fuel oil prices were low. Many of the new laterite treatment plants built in this period became uneconomic after the oil price increase in 1973, and as a result there was little or no increase in the proportion of nickel produced from oxide ores between 1975 and 1990.

Several international mining industry consortia evaluated the feasibility of recovering nickel from deep sea manganese nodules during the 1970s, and potential mining techniques were developed and tested. However, processing of the nodules to separate and recover the metals proved to be significantly more expensive than for land-based ores [15, 16]. The international legal aspects of ownership of these deep sea resources were the subject of the 11th Session of the Third U.N. Conference on the Law of the Sea, which ended in April 1982 with only a partial agreement which several major participants refused to sign [17]. These developments, in conjunction with low nickel prices, essentially killed any serious consideration of deep sea nodules as a source of nickel

during the 1980s. Development of this resource on a significant scale is therefore unlikely before the next century.

12.3 Beneficiation of Nickel Sulfide Ores [1, 18]

The low metal content of present-day nickel sulfide ores renders them unsuitable for either direct smelting or direct hydrometallurgical processing. Because the sulfide minerals usually occur as distinct grains in the rock matrix, these ores are amenable to a mechanical upgrading in which much of the rock content can be rejected. The metal content of the ore is concentrated by a physical treatment such as comminution to liberate the metal sulfide grains, followed by froth flotation or magnetic separation to recover a metal-rich concentrate [19].

In principle it is possible to produce separate nickel (pentlandite), copper (chalcopyrite), and iron (pyrrhotite) concentrates. However, a clean separation of pentlandite from pyrrhotite is difficult in practice since pyrrhotite typically contains intergrown inclusions of pentlandite as well as nickel in solid solution in the pyrrhotite. In fact pyrrhotite often contains 0.5–1 % Ni that cannot be separated by physical methods. The relatively high nickel content in pyrrhotite makes it difficult to achieve high yields of nickel from the ore unless the pyrrhotite is processed to recover its nickel content, and conversely the presence of nickel makes it difficult to obtain a marketable iron product from the pyrrhotite.

Most nickel producers, outside Canada, make no attempt to obtain separate nickel, copper, and iron concentrates and produce a bulk concentrate that contains pentlandite, pyrrhotite, and chalcopyrite as smelter feed. In Canada, both the major producers separate a large part of the pyrrhotite from pentlandite and chalcopyrite, and Inco further separates the pentlandite and chalcopyrite into separate nickel and copper concentrates. Even where the bulk of the pyrrhotite can be separated from pentlandite, residual pyrrhotite in the

nickel concentrate still contributes a major part of the sulfur content.

In response to ever tighter constraints on sulfur dioxide emissions from smelters during the 1970s and 1980s, the Canadian companies have made increased pyrrhotite rejection from smelter feed a major priority, and substantial improvements have been achieved. A pyrrhotite concentrate was treated by Inco for many years for nickel and iron oxide recovery. However, current environmental constraints on sulfur dioxide emissions have rendered the process obsolete, and pyrrhotite concentrates are now largely stockpiled, since none of the known treatment methods that avoid sulfur dioxide production is economic.

Pyrrhotite can be separated from pentlandite and chalcopyrite either by using its ferromagnetic properties or by flotation. Not all pyrrhotite is ferromagnetic, although in ores from the Sudbury, Ontario area the magnetic monoclinic form predominates over the paramagnetic or "nonmagnetic" hexagonal form [20]. In general, pyrrhotite containing less sulfur than $\text{Fe}_{0.87}\text{S}$ is nonmagnetic. This material can usually be separated from pentlandite by flotation.

Nickel or nickel copper concentrates typically range in grade from 5 to 15 % Ni + Cu, depending on the degree of pyrrhotite rejection achieved. An exceptionally high-grade concentrate, containing 28 % Ni and consisting largely of pentlandite, is produced in limited amounts at Inco's Thompson, Manitoba operation.

One of the more complex nickel concentration process flow sheets is that operated by Inco at its Sudbury operation [21]. In the two primary concentrators, the Clarabelle mill and the Frood-Stobie mill, 50 000 t/d of ore, grading 1.2 % Ni and 1.2 % Cu, is ground to a particle size of ca. 200 μm and treated by magnetic separation and flotation with a sodium amyl xanthate reagent to produce 5000 t/d of a bulk nickel copper concentrate and 8000 t/d of a pyrrhotite concentrate. Metallurgical data for the Clarabelle mill are given in Table 12.4.

Table 12.4: Metallurgical data for the magnetic separation and flotation of nickel ore (Clarabelle mill, Inco) [21].

	%	Analysis, %			Recovery, %		
		Cu	Ni	Pyrrhotite	Cu	Ni	Pyrrhotite
Ore	100	1.32	1.40	18.9	100	100	100
Magnetic concentrate	26	0.62	1.65	62.7	12	30	84
Flotation concentrate	8	14.4	11.6	15.9	84	64	7
Tails	66	0.07	0.13	2.5	4	6	9

Table 12.5: Metallurgical data for the upgrading of pyrrhotite and copper–nickel concentrate (Copper Cliff mill, Inco) [21].

	%	Analysis, %			Recovery, %		
		Cu	Ni	Pyrrhotite	Cu	Ni	Pyrrhotite
Feed	100	4.58	4.42	49.6	100	100	100
Copper concentrate	13	29.2	0.91	8.4	83	3	2
Nickel concentrate	29	2.28	12.8	43.0	14	85	25
Pyrrhotite concentrate	33	0.11	0.96	84.4	1	7	57
Tails	25	0.36	0.91	32.3	2	5	16

The two primary concentrates are further upgraded in the Copper Cliff mill. The bulk nickel copper concentrate is separated by flotation into separate nickel and copper concentrates by using lime and sodium cyanide at 30–35 °C to depress pentlandite and pyrrhotite. Under these conditions about 92 % of the copper is recovered to a concentrate grading 29 % Cu and 0.9 % Ni. About 98 % of the nickel and 92 % of the pyrrhotite are rejected to the separator tails, which grade 13 % Ni and 2 % Cu.

The Clarabelle rougher pyrrhotite concentrate is treated to separate residual chalcopyrite and pentlandite by grinding to ca. 74 μm followed by magnetic separation and flotation. A magnetic, cleaner pyrrhotite concentrate, a bulk nickel copper concentrate, and a nonmagnetic pyrrhotite tail are produced. The nonmagnetic tails stream (1 % Cu, 2 % Ni, and 30 % pyrrhotite) is further treated, by regrinding and flotation in the pyrrhotite rejection circuit, for final recovery of pentlandite and chalcopyrite before it is discharged to the tailings pond. Overall, about 80 % of the pyrrhotite content of the ore is rejected from smelter feed to the pyrrhotite concentrate and tails. Metallurgical data for the Copper Cliff mill are given in Table 12.5.

Falconbridge at its Strathcona mill in the Sudbury basin treats ore containing 1.5 % Ni and 1.1 % Cu by grinding and flotation to produce a nickel copper concentrate grading

6.7 % Ni and 5.6 % Cu at an average recovery of 83 % Ni and 93 % Cu [22–24]. A large part of the pyrrhotite content of the ore is rejected directly to the tailings pond. The separation of the nickel and copper in the bulk concentrate is carried out in the matte refining process after smelting.

The ore mined by Inco at Thompson, Manitoba consists of pentlandite and pyrrhotite with only a small amount of chalcopyrite (2.7 % Ni, 0.2 % Cu, 22 % pyrrhotite). Since the pyrrhotite contains 78 % of the sulfur but only 5.5 % of the nickel, a high degree of pyrrhotite rejection is feasible without seriously decreasing the nickel recovery [25]. The ore is ground and floated to recover a nickel copper concentrate and reject 90 % of the gangue and 60 % of the pyrrhotite to tails. The nickel copper concentrate is treated by flotation to separate first a copper concentrate, and then by magnetic separation and flotation to recover a high-grade (28 % Ni) pentlandite concentrate. The tailings stream from these steps forms the main nickel concentrate smelter feed (11 % Ni, 0.4 % Cu). The overall recovery of nickel to the nickel and pentlandite concentrates is about 87 %, while another 5 % of the nickel reports to the copper concentrate. Over 60 % of the pyrrhotite is rejected to tailings with only 8 % of the nickel.

At the BCL nickel–copper mine in Botswana the pyrrhotite/pentlandite ratio in

the ore averages about 13:1 and the pyrrhotite contains over 30% of the nickel either in solid solution or as small pentlandite inclusions. Consequently, high nickel recoveries can only be achieved by recovering the nickel from pyrrhotite. This is achieved by producing a bulk pentlandite-pyrrhotite-chalcopryrite concentrate, with a typical composition of 2.8% Ni and 3.2% Cu [26]. Modern nickel concentrators are largely automated and are equipped with process control systems based on on-line X-ray analysis of process streams [27].

12.4 Pyrometallurgy of Nickel Concentrates

Over 90% of the world's nickel sulfide concentrates are treated by pyrometallurgical processes to form nickel-containing mattes [1, 28–32]. Production capacities and composition of the feed concentrate and product matte are listed in Table 12.6 for several major nickel smelters.

The pyrometallurgical treatment of nickel concentrates includes three types of unit operation: roasting, smelting, and converting. In the roasting step sulfur is driven off as sulfur dioxide and part of the iron is oxidized. In smelting, the roaster product is melted with a siliceous flux which combines with the oxidized iron to produce two immiscible phases, a liquid silicate slag which can be discarded, and a solution of molten sulfides which contains the metal values. In the converting operation on the sulfide melt, more sulfur is driven off as sulfur dioxide, and the remaining iron is oxidized and fluxed for removal as silicate

slag, leaving a high-grade nickel copper sulfide matte.

In several modern operations the roasting step has been eliminated, and the nickel sulfide concentrate is treated directly in the smelter.

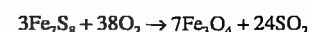
12.4.1 Roasting

Roasting [33] is basically a process in which the nickel sulfide concentrates are heated in an oxygen-containing gas, usually air, to a temperature (600–700 °C) at which oxygen oxidizes sulfide to sulfur dioxide and reacts with the metal values to form solid oxides, termed the calcine. The roasting step may also serve to preheat the charge for smelting.

The thermodynamic relationships between the metal sulfides and oxides provide the basis for the separation of iron from nickel, copper, and cobalt contained in the concentrate. The sulfides of iron, nickel, cobalt and copper are all in the same thermal stability range at the smelting temperatures (1200–1300 °C), but, in the presence of oxygen, each sulfide is unstable with respect to its corresponding oxide. Iron has the greatest affinity for oxygen, followed by cobalt, nickel, and copper. Consequently, if the nickel concentrate is roasted with a deficiency of oxygen the iron is oxidized preferentially, while virtually all of the nickel and copper remain as sulfides. Thus the degree of oxidation of the charge and the degree of elimination of sulfur can be controlled by regulating the supply of air to the roaster.

The degree of sulfur elimination achieved in the roasting step largely determines the grade of the matte produced as well as the losses of nickel and copper to the slag phase in the subsequent smelting operation. All the sulfur present in the calcine in excess of the amount needed to combine with the nickel, copper, and cobalt in the matte combines with iron, which therefore remains in the matte phase and lowers its nickel copper cobalt grade. The major constraint on achieving a high-matte grade in smelting is the increasing loss of nickel, copper, and cobalt to the slag phase. If all of the iron were to be oxidized in the roasting step so that it could be slagged off in the smelting stage and a high-grade matte produced directly, an increased amount of nickel, copper, and cobalt oxides would be formed in the roaster, and metal losses to the slag in smelting would increase substantially. Hence, each smelting operation seeks to operate at an optimum matte grade which gives the highest metal value recovery to the matte. The balance of the iron is removed in the converting step.

Normally only about 50% of the pyrrhotite content of the nickel concentrate is oxidized in roasting, and under these conditions less than 5% of the nickel and copper are oxidized, with the balance remaining as sulfides. The oxidation of pyrrhotite to magnetite can be represented by the following reaction:



This reaction is strongly exothermic, and autogenous roasting, without the use of an external heat source, is practiced whenever possible.

In order to achieve effective roasting the furnace must provide good contact between the sulfide particles and the oxygen-bearing gas. The furnace system must also be able to provide close control of the degree of sulfur elimination. Both multihearth roasters and fluidized-bed roasters are in current industrial use for nickel concentrate roasting. The use of traveling grate sintering machines, which were formerly widely used to prepare an agglomerated feed for blast furnace smelting, is

now practiced only in the former Soviet Union.

The multihearth roasting furnace consists of a series of vertically superimposed circular hearths. Wet concentrate and smelting flux are charged to the upper hearth. A central rotating shaft drives rabble arms that extend across the roaster hearths, turning over the concentrate charge and transferring it via dropholes to the next lower hearth. Air, preheated by the combustion of natural gas, passes upwards through the hearths, heating the concentrate to ignition temperature and providing the oxygen required to burn the concentrate. The temperature is controlled by regulating the flow of air into the roaster.

Since the area of contact between the furnace gas and concentrate particles on the hearths is very limited, the total time required for roasting in this type of furnace is long, resulting in low throughput rates. A further disadvantage of the multihearth roaster is that low oxygen utilization and high air infiltration rates produce an off-gas with a low concentration of sulfur dioxide which is unsuitable for sulfuric acid production.

Multihearth roasters are still used in the Copper Cliff smelter of Inco in Ontario, which was built in 1930. A battery of 24 roasters can each treat 300 t/d of wet concentrate mixed with 75–90 t/d of siliceous flux. About 40% of the sulfur content of the concentrate (13% Ni, 2–3% Cu, 30% S, and 40% Fe) is eliminated at a roasting temperature of 800 °C. Less than 5% of the nickel and copper are oxidized. This operation is not thermally self-sustaining, due to high heat losses from the roaster, and natural gas is used to provide supplementary heating. The off-gas is cleaned to recover dust and is vented to a stack. The roasted calcine discharge from the bottom of the furnaces is conveyed directly to the reverberatory smelting furnaces [34].

The fluidized-bed roaster is a more recent development and has an improved gas solids contact efficiency and a simpler construction (Figure 12.2). The roasting furnace is a vertical chamber of circular cross section with a grate hearth through which the oxygen-bearing

Table 12.6: Nickel sulfide smelters [30–32].

Smelter	Feed concentrate, %		Matte product, %		Nominal capacity, t/a Ni
	Ni	Cu	Ni	Cu	
Inco, Copper Cliff	13	2.7	63	15	110 000
Inco, Thompson	10.5	0.4	73	3	50 000
Western Mining	11.4	0.85	72	5	60 000
Falconbridge	6.7	5.6	40	34	45 400
Outokumpu	8–9	2–4	64	26	18 000
BCL, Botswana	2.8	3.2	38	40	20 000
Rustenburg	3.2	2.0	47	27	19 000
Bindura	10.6	3.4	70	20	14 400

ing gas is blown. As nickel concentrate and smelting flux are fed to the chamber, the particles are suspended in the vertical air flow. Since each sulfide particle is in constant turbulent motion in the oxidizing atmosphere, roasting is uniform and rapid, with efficient heat transfer and oxygen utilization. Solids are discharged from the furnace either by overflow through a side port or by entrainment in the off-gas stream. The dust-laden gas may be passed through waste-heat boilers to recover its sensible heat. The cleaned off-gas stream contains a high concentration of sulfur dioxide, which can be converted to sulfuric acid.

Fluidized-bed roasting of nickel concentrates is practiced by Inco at the Thompson smelter in Manitoba and at Copper Cliff, where 10% of the nickel concentrates are processed in fluidized-bed roasters, and by Falconbridge at its smelter in Ontario. The Thompson smelter operates five fluidized-bed roasters with a combined capacity of 3800 t/d of concentrate, while the Falconbridge smelter operates two roasters with a combined capacity of 2000 t/d of concentrate [22, 35].

In the Falconbridge smelter a slurry (75% solids) of nickel-copper concentrate (6.7% Ni, 5.6% Cu, 30% S, 40% Fe) in water is fed directly to the roaster. Siliceous flux is added separately. Sulfur elimination ranges from 50 to 60% at a roasting temperature of 600–650 °C. The operation is thermally autogenous, and the water contained in the feed slurry serves as a heat sink to control the bed temperature. Oxygen utilization is essentially 100%. About 85% of the calcine leaves the roaster in the off-gas stream which is treated in a series of cyclones, gas coolers, and electrostatic precipitators for solids recovery. The solids recovered from the gas cleaning system are combined with the coarser roaster bed overflow calcine, for charging to the electric smelting furnaces [24].

12.4.2 Smelting

In the treatment of nickel sulfide ores and concentrates the function of the smelting process is to eliminate the gangue minerals and

most of the iron sulfide and to concentrate the metal values into a high-grade nickel-copper matte containing 0.5–3.0% Fe and 6–22% S. Unlike copper, nickel metal cannot be produced by the oxidation of the sulfide at a practical smelting temperature (up to ca. 1400 °C).

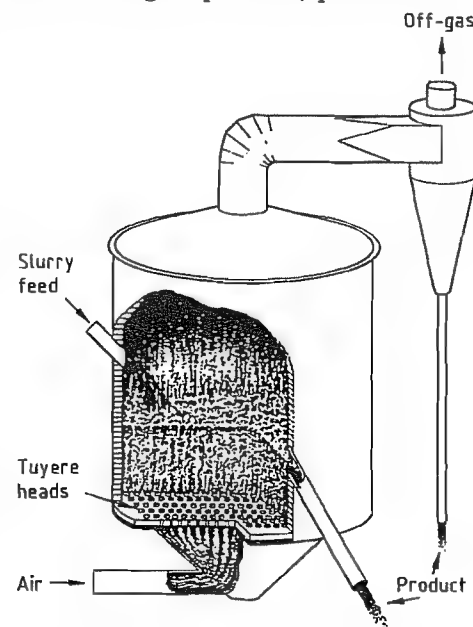


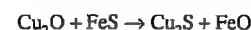
Figure 12.2: Cutaway view of a fluidized-bed roaster.

When a mixture of metal sulfides, iron oxide, gangue, and siliceous flux are melted together, the iron oxide, gangue, and silica form a slag layer that floats on the heavier, molten sulfide or matte phase. The two immiscible layers are separated and the slag is discarded.

The smelting process for nickel sulfide concentrates is normally carried out in two stages: primary smelting and converting. The oxidizing, slagging, and removal of iron in stages is critical to the efficiency and economics of smelting operations. If most of the iron were to be oxidized in the roaster and then slagged in a single smelting step, a matte high in nickel and low in iron would be produced. However, as noted above, significant amounts of the nickel and copper sulfides would also be oxidized in the roaster, and these oxides would be lost to the slag in the smelting step. Slag can also mechanically entrain droplets of

matte and these losses will also increase with matte grade. Thus if a high-grade matte were to be produced in one step, the overall recovery of nickel would be low.

Provided that only about half the iron is oxidized in the initial roasting step, only 5% of the nickel and copper sulfides are oxidized. In fact only a small amount of these oxidized metals will be lost to the slag because the oxides react with residual iron sulfides in the smelting process to produce the corresponding sulfides, which return to the matte phase.



Thus a low-grade, high-iron furnace matte is produced and only a small amount of nickel is lost to the slag as oxide when the nickel concentrate is treated in separate roasting and smelting steps.

The iron remaining in the furnace matte is oxidized and slagged in the secondary smelting step (converting). Since the slag produced in the converting stage, in which a high-grade, low-iron matte is produced, has a high nickel and copper content, it is returned to the primary smelting stage where the metal values are recovered by the reaction of the oxides with iron sulfide and by the settling of entrained droplets of matte. Thus the two-stage smelting process allows the production of a high-grade, low-iron nickel matte, and a high-iron slag of low metal grade which can be discarded without significant loss of metal values.

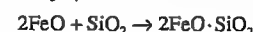
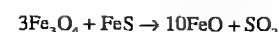
12.4.2.1 Primary Smelting

The primary smelting step is carried out in a variety of furnaces, including reverberatory, electric, and flash furnaces, which provide a wide variety of smelting conditions. Chemical losses of nickel and copper to the slag increase with the oxidation potential of the system. Thus metal losses to slag are much higher in the flash smelting furnace, in which the roasting step is combined with the primary smelting step, and smelting conditions are strongly oxidizing, than in the electric furnace, where

smelting is carried out under reducing conditions. Consequently, slag from the flash smelting process must be treated in a separate step to recover the contained metal values, while slag from the electric furnace or reverberatory furnace smelting processes can be discarded without further treatment.

A typical furnace matte containing 10% Ni, 65% Fe, and 25% S melts at ca. 950 °C, and nickel sulfide itself melts at ca. 790 °C. The melting point of a fayalite slag with an iron to silica ratio of about 7:3 is 1200 °C, although the slag melting point can be reduced to 1100 °C by the addition of a few percent of lime and alumina. With this type of slag, smelting is carried out at ca. 1200 °C. However, when significant levels of magnesia are present in the nickel concentrate or ore the melting point of the slag may be as high as 1260 °C, and smelting is then carried out at ca. 1400 °C [36–38].

Magnetite, which is formed in the partial roasting of the concentrates, reacts in the primary smelting step with the remaining iron sulfides and silica flux to form fayalite:



The presence of magnetite in slags and mattes not only affects the chemistry of the smelting operation, but has an important effect on the smelting furnace. Magnetite is formed under strongly oxidizing conditions and its formation is favored by low operating temperatures and by silica-deficient slags. The magnetite content of slags from the more oxidizing reverberatory and flash smelting furnaces is usually above 10%, with the content increasing with matte grade, while slags from reduction smelting electric furnaces typically contain less than 5% magnetite. Magnetite tends to settle out in the bottom of the smelting vessel and accretions can severely reduce the operating capacity of the furnace. Consequently it is always desirable to minimize the formation of magnetite in the smelting process.

Reverberatory Furnace Smelting. In the reverberatory furnace, fossil fuel (pulverized

coal, oil, or natural gas) is burned separately from the material being smelted. The furnace is a long rectangular structure with an arched roof and burners at one end and in the roof. A large part of the heat from the combustion gas radiates directly to the charge lying in the hearth below. A further substantial part of the heat is reflected from the walls and roof of the furnace into the charge. Solid charge is fed through vertical fettling pipes mounted in the roof along each side of the furnace. As the charge melts it flows towards the center of the furnace. Molten converter slag is introduced into the furnace at the firing end.

Slag is tapped from the end of the furnace opposite the burners, while matte is tapped from the side. This type of furnace has a low energy efficiency since the off-gas stream carries nearly 50% of the heating value of the fuel. Waste-heat boilers or heat exchangers are used to recover heat from the off-gases.

The reduction of the magnetite formed in the roaster to ferrous oxide is not complete in the reverberatory furnace, and slags contain up to 7% magnetite. Scrap iron or ferrosilicon is often added to control the formation of magnetite to minimize metal losses to the slag and to prevent magnetite buildup in the furnace hearth.

Inco uses two reverberatory furnaces equipped with roof-mounted oxyfuel burners for the primary smelting of nickel concentrates at its smelter in Copper Cliff, Ontario. Each furnace treats 1500 t/d of partially oxidized concentrate (13% Ni, 2.7% Cu) which is transferred at 700 °C from the multihearth roasters, together with 700 t/d of recycled molten converter slag. Oxygen enrichment of the combustion air supplied to the oxyfuel burners not only increases fuel utilization efficiency but also substantially increases the capacity of the furnace [34, 39–43].

The furnace matte contains 30–35% nickel plus copper, together with the precious metals content of the charge. The reverberatory slag, which normally analyzes 0.2% Ni, 0.1% Cu, 0.1% Co, 38% Fe, and 36% SiO₂, is discarded. The matte is tapped at 1150 °C and blown with oxygen-enriched air (30% O₂), in

one of 14 Peirce–Smith converters, to a high-grade, sulfur-deficient matte containing 78% Ni and Cu and 20% S. The converter slag, typically containing 2.3% Ni and Cu, 50% Fe, and 25% SiO₂, is recycled to the reverberatory furnace for recovery of the contained nickel and copper [42].

Electric Furnace Smelting. The energy required for smelting may be obtained from electrical power as an alternative to burning fossil fuels or sulfides in air or oxygen. The use of an electric furnace for nickel sulfide smelting is favored when the cost of electrical energy is low or when the required smelting temperature is high, for example, when the concentrate contains high levels of magnesia.

Heating of the bath is achieved by passing a three-phase electrical current through a circuit consisting of carbon electrodes immersed in the slag layer, which has a high electrical resistance (submerged arc technique). Electric furnaces used for nickel–copper matte smelting are either rectangular with six electrodes in line or circular with three electrodes in triangular configuration. The consumable electrodes are made of carbon and are either prebaked or are of the self-baking Söderberg type.

The charge of concentrate (or calcine) and flux is fed through the roof. Thus a layer of unsmelted charge covers the slag giving it a “cold top”. The concentrate or calcine gradually settles into the slag as it melts and then separates into slag and matte layers. The slag and matte are tapped intermittently, as required. Since there is no fuel combustion in an electric furnace the quantity of off-gas is much less than from a reverberatory furnace and heat and dust recovery from the off-gas is therefore easier.

Electric furnace smelting of nickel concentrates is practiced by Inco at its Thompson, Manitoba, operation; by Falconbridge at Sudbury, Ontario; by the Severonikel Combine in the former Soviet Union; by Rustenburg Platinum, Impala Platinum, and Western Platinum in the Republic of South Africa; and by Bindura Nickel in Zimbabwe. The Canadian oper-

ations treat partly roasted concentrate calcines, while Bindura and the platinum producers treat nickel–copper concentrates directly. The Severonikel electric furnace smelter treats high-grade ore from Norilsk (3.5% Ni, 3.5% Cu) directly [44]. Current industrial practice is illustrated by the following examples.

In the Rustenburg Refiners smelter [45] in the Republic of South Africa, pelletized nickel–copper concentrate, containing 3.2% Ni, 2% Cu, 15% Fe, 39% SiO₂, 15% MgO, 3% CuO, 6% Al₂O₃, 9% S, and ca. 130 g/t precious metals, is mixed with a lime flux and smelted directly in a 19.5 MVA electric furnace. About 98% of the nickel and 97% of the copper and most of the precious metals contained in the concentrate are recovered to a matte containing about 17% Ni, 10% Cu, 40% Fe, and 27% S. The electric furnace slag, containing 0.1% Ni and 0.06% Cu, is tapped at 1350 °C and discarded. The matte is tapped at 1180 °C and converted in Peirce–Smith converters to a product analyzing 48% Ni, 27% Cu, 1.5% Fe, and 20% S, again with high recovery of the precious metals to the matte.

The Falconbridge smelter in Sudbury, Ontario, which was built in 1978 on similar lines to Inco's Thompson smelter, is a good example of the modern large-scale application of fluidized-bed roasting and electric furnace smelting of nickel–copper concentrates (Figure 12.3). The smelter contains two roaster electric furnace lines, each of which was de-

signed to treat up to 1250 t/d of nickel–copper concentrate (6.7% Ni, 5.6% Cu). The electric furnaces are each rated at 33 MVA and have a six-in-line electrode configuration. The electrodes are of the Söderberg self-baking type. Typical furnace operating conditions are as follows [21, 46, 47]:

Concentrate feed rate	900 t/d
Power consumption	1.2 GJ/t solid charge
Slag temperature	1230 °C
Matte temperature	1130 °C
Off-gas temperature	700 °C
Calcine depth	500 mm
Slag depth	1500 mm
Matte depth	700 mm
Bottom buildup	150 mm
Electrode immersion	250 mm
Off-gas volume	28 300 m ³ /h (STP)

Roaster calcine together with the flux added prior to roasting, at about 600 °C, is conveyed directly to the furnace and added to the bath through fettling tubes mounted in the furnace roof. Recycle dusts and scrap together with reductants are added to the calcine conveyors. Converter slag is fed to the furnace through a launder above the matte-tapping end of the furnace.

Coke is added to the charge as a reductant, at a rate of 2.5% of the concentrate, to improve metal recoveries and to reduce magnetite formation. The use of coke reductant and operation of the furnace under “black top” conditions results in a significant power saving compared with open-bath operation under oxidizing conditions (1.2 GJ/t versus 1.5 GJ/t of solid charge).

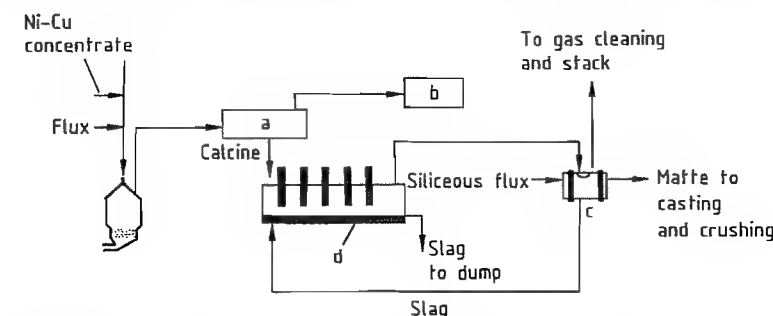


Figure 12.3: Flow sheet of the Falconbridge smelter: a) Gas-scrubbing and calcine recovery; b) Acid plant; c) Converter; d) Electric furnace.

The electric furnace slag, typically containing 0.12% Ni, 0.20% Cu, and ca. 4% magnetite, is tapped at 1230 °C and is transferred in slag pots to a disposal area. The furnace matte, which normally contains 24% Ni + Cu, is tapped at 1130 °C and is transferred to one of four Peirce-Smith converters where it is blown with air to produce a matte containing 74% Ni + Cu, 1% Co, 2.5% Fe, and 23% S. The converter matte is cast, crushed, and shipped to the Falconbridge refinery in Norway. The converter slag is recycled to the electric furnace, and the converter off-gases are cleaned in electrostatic precipitators and vented to a stack.

Flash Smelting. In flash smelting, a finely ground sulfide concentrate is smelted by burning some of its sulfur and iron content while the sulfide particles are suspended in the oxidizing atmosphere. The concentrate is roasted and smelted in a single process step. The predried concentrate and flux materials are injected with preheated oxygen-enriched air or commercial oxygen into the reaction shaft of a specially designed furnace. The exothermic heat of reaction of the iron sulfide with oxygen provides the energy to heat the particles to smelting temperature. The smelting temperature and the grade of matte formed are both controlled by adjusting the ratio of the amount of oxygen supplied to the furnace to the throughput rate of concentrate. In current practice, which uses oxygen-enriched air, the process can be thermally autogenous, and the addition of a fossil fuel is not generally required.

The flash smelting process was developed independently by Inco in Canada and Outokumpu in Finland, shortly after World War II. In both cases it was applied commercially to the treatment of copper concentrates. The Inco process uses commercial oxygen (95%) while the Outokumpu process initially used air, augmented by fuel oil, as the oxidant and energy sources. The Outokumpu process was first applied commercially to the treatment of nickel concentrates in 1959. Oxygen enrichment of the combustion air was introduced by Outo-

kumpu in 1971 and resulted in several major improvements in furnace performance. The Inco flash smelting process was successfully tested on a full production scale for the treatment of nickel concentrate in 1976, and will be utilized in the modernization of the Copper Cliff smelter scheduled for the early 1990s. In addition to its own installation at Harjavalta in Finland, the Outokumpu flash smelting process for nickel has been adopted by the Western Mining Corporation in Australia, by BCL in Botswana, and by the Norilsk Combine in Russia. The Outokumpu flash smelting process for copper has been adopted in about 30 operations worldwide [48, 49].

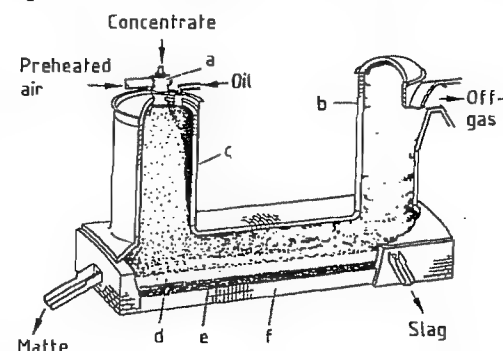
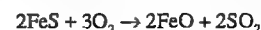


Figure 12.4: Cutaway view of an Outokumpu flash smelting furnace: a) Concentrate burner; b) Uptake; c) Reaction shaft; d) Slag; e) Matte; f) Settler.

The Outokumpu flash smelting furnace, essentially an upright U in shape, consists of a vertical reaction shaft, a horizontal reverberatory settler hearth, and a vertical gas uptake shaft (Figure 12.4). Predried nickel concentrates and fluxes are mixed with oxygen-enriched air and injected into the furnace by means of the concentrate burner mounted at the top of the reaction shaft. The resulting suspension spreads over the area of the reaction shaft. At operating temperatures, ignition of the iron sulfides occurs instantly, and the following exothermic reaction with oxygen provides all the heat required for smelting:



The nickel and copper sulfides melt to form a matte, while the iron oxide combines with silica flux to form a fayalite slag. Separation

of the molten particles from the combustion gases occurs as the gas stream leaves the reaction shaft. The melt collects in the settler, where the matte and slag form separate layers and are tapped at opposite ends of the furnace.

Nickel flash furnace mattes typically grade 50–55% Ni + Cu, and the grade is controlled by adjusting the ratio of oxygen to concentrate in the furnace. The furnace mattes are treated in Peirce-Smith converters with oxygen-enriched air to produce a high-grade matte product. The converter slag is either recycled to the flash furnace or treated directly in a slag cleaning furnace to recover the contained metal values. The composition of converter matte varies between smelters. The final sulfur content is adjusted in accordance with the requirements of the subsequent refining process. Thus at Harjavalta the matte is blown to a sulfur content of only 4–7%, while the other smelters produce matte containing about 20% S.

When oxygen-enriched air is used to produce a high-grade furnace matte, operating temperatures are sufficiently high to reduce magnetite formation and prevent significant magnetite accretions building up in the furnace. Inevitably, when a high-grade matte is produced under oxidizing conditions the slags contain too high a level of metal values to be discarded. Nickel flash furnace slags are generally cleaned by reduction and settling in an electric furnace, with coke as the reductant. The Western Mining flash furnace in Australia has been modified by the extension of the settler beyond the gas uptake shaft [50, 51]. This extension to the settler hearth contains two sets of electrodes and serves as a continuous slag cleaning furnace. The furnace slag tapped from the extension is sufficiently low in metal values to be discarded. At the BCL smelter in Botswana, which treats a very low-grade concentrate and consequently has a high slag to matte ratio, slag losses are controlled in the settler itself by the addition of lump coal, which floats on the surface of the slag and reduces the metal oxides [26, 52]. The slag is further cleaned in two electric furnaces connected in series before being discarded. Re-

cent metallurgical data for three flash smelting operations are presented in Table 12.7.

Off-gases leave the flash furnace through the uptake shaft and enter a waste-heat boiler where the heat content of the gas is recovered as high-pressure steam. The gas, which has a high sulfur dioxide content, is cleaned in electrostatic precipitators to recover entrained dust. The cleaned gas stream can be used as a feed to a sulfuric acid plant, for liquid sulfur dioxide recovery, or can be reduced to elemental sulfur with a fossil fuel.

The flash smelting process is particularly suited to the application of automated process control. The major control parameter is the ratio of oxygen in the combustion air to concentrate throughput. This parameter not only controls the degree of oxidation of the sulfides but also the grade of the matte and the operating temperature. The process is thus controlled by adjusting the flow rates of both combustion air and commercial oxygen, in relation to the concentrate feed rate. The slag composition is controlled by the rate of addition of flux materials to the concentrate in the furnace feed blend. Control of the process can thus be fully computerized [53].

Table 12.7: Metallurgical data for flash smelters [50–53].

Smelter		Outokumpu	Botswana	Western Mining
Capacity, t/a concentrate		190 000	800 000	600 000
Concentrate, %	Ni	8–9	2.8	11.4
	Cu	2–4	3.2	0.9
	Fe	24–27	43.5	38
	S	19–22	31.0	32
Furnace matte, %	Ni	33	15	44
	Cu	19	17	3
	Fe	18		27
	S	25		22
Converter matte, %	Ni	58	36	72
	Cu	32	40	5
	Fe	0.5	<1	<1
	S	6	20	21
Discard slag, %	Ni	0.15	0.15	0.28
	Cu	0.32	0.34	0.08
Smelter recovery, %		95	91.5	96

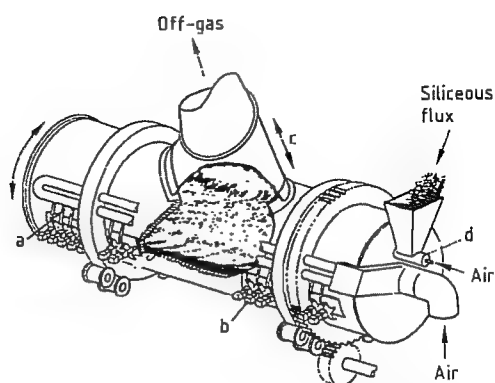
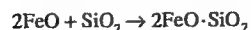
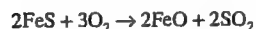


Figure 12.5: Cutaway view of a Peirce-Smith side blown converter: a) Tuyere pipes; b) Pneumatic punchers; c) Hood; d) Flux gun.

12.4.2.2 Matte Converting

In the converting step [54–56], iron sulfide is removed from the molten, low-grade furnace matte by oxidation and slagging. The slag, which contains high levels of nickel and copper, is returned to the primary smelting furnace for recovery of metal values. The high-grade, low-iron nickel-copper matte, which typically contains 20% S, less than 1% Fe, and also any precious metals present in the original concentrates, is the final product of the smelting process.

Converting is a batch operation. The horizontal side blown converter, known as the Peirce-Smith converter (Figure 12.5), is normally used for the treatment of nickel furnace mattes, although top blown rotary converters are used in some modern plants, particularly for low production rates. Air or oxygen-enriched air is blown through the molten matte to form iron oxides and remove sulfur as sulfur dioxide. The iron oxides combine with added silica flux to form an iron silicate slag:



A substantial amount of magnetite is also formed in the conversion process.

Converter slags contain 20–35% silica, with the balance being iron oxides. Silica in the slag combines with iron(II) oxide, thus preventing further oxidation to magnetite.

Slags low in silica contain large amounts of magnetite. Typically, up to one-third of the iron may be in the iron(III) state in a 20% silica slag, while a slag with 35% silica contains less than 15% magnetite. Magnetite formation is useful in converting since it can be made to coat the inside of the brick-lined furnace and thus protects it from erosion and corrosion by the slag [57, 58].

The oxidation of iron sulfide is strongly exothermic and much of the heat generated in the conversion process can be utilized to melt additional ore or concentrate feed or recycled scrap materials. Since the throughput of a converter is almost directly proportional to the amount of oxygen blown through the charge, its capacity can be raised substantially by enriching the air with oxygen. In addition to increasing the converting rate, oxygen enrichment of the air permits the treatment of additional cold charge, and in fact the addition of cold charge is essential to control the bath temperature when oxygen-enriched air is used. Up to 3 t of cold charge materials can be smelted for each tonne of oxygen supplied.

12.4.3 Environmental Aspects of Nickel Smelting

During the 1970s and 1980s the nickel industry responded to increasing public concern over smelter emissions of sulfur dioxide to the environment by replacing outdated process equipment, such as multihearth roasters, sinter machines, blast furnaces, and reverberatory furnaces, by processes such as fluidized-bed roasting, electric furnace smelting, and flash furnace smelting, which are more energy efficient and environmentally cleaner.

However, while the technology is available to produce sulfuric acid economically from sulfur dioxide in the high-strength off-gas streams produced by the modern smelting techniques, there is not always a market for large amounts of acid within an economic shipping distance of the nickel smelter. Thus, although the Inco and Falconbridge smelters in the Sudbury area of Ontario do convert a substantial amount of their sulfur dioxide to

acid, more remote operations, including Inco's smelter at Thompson, Manitoba, Western Mining's smelter in Western Australia, and the BCL smelter in Botswana, vent SO_2 -containing off-gases to the atmosphere. In fact the BCL smelter was designed with the capability to convert sulfur dioxide to elemental sulfur by reduction with fuel oil. However, this process proved uneconomic when oil prices increased in the early 1970s and it has never been operated. A similar circuit that uses natural gas to reduce sulfur dioxide to sulfur is in operation at the Norilsk flash furnace smelter in the former Soviet Union, which was commissioned in 1981 [58].

A more cost-effective method of reducing sulfur dioxide emissions is to reject as much pyrrhotite as possible from the smelter feed by separating pyrrhotite from pentlandite in the concentrator. As much as 50–60% of the pyrrhotite content of the ore is now rejected in the major Canadian nickel operations at Sudbury and Thompson. At Thompson, Inco reduced SO_2 emissions by 45% between 1976 and 1986 simply by increasing pyrrhotite rejection, but incurred significant metallurgical penalties by doing so [25]. Not only was the overall recovery of nickel reduced but the absence of much of the pyrrhotite removed a major energy source for the smelting process. Since the roasting and converting steps were designed to be autogenous using the iron sulfide as fuel, when over 50% of the pyrrhotite is rejected prior to smelting insufficient iron is available to sustain the converting operation, and extra fuel must be supplied.

Maximum pyrrhotite rejection is practiced by both Inco and Falconbridge at their Sudbury operations. In these ores the nickel content of the pyrrhotite mineral is higher than in the Thompson ore and so pyrrhotite rejection results in significant losses in nickel recovery. A process to treat pyrrhotite concentrate separately to recover nickel, iron ore, and sulfuric acid, was operated by Inco for many years but the operation was abandoned in the mid 1980s when it became uneconomic due to increasingly stringent sulfur emission limits [32].

Falconbridge rejects over 55% of the pyrrhotite in its ore and recovers sulfuric acid from the sulfur dioxide in the fluidized-bed roaster off-gas stream. Electric furnace and converter off-gases are vented to the atmosphere as a low-strength sulfur dioxide stream. The distribution of sulfur in the Falconbridge operation in 1983 is detailed in Table 12.8 [24, 52].

Table 12.8: Sulfur distribution at Falconbridge, Sudbury, Ontario in 1983 [24].

	Sulfur, t/d	Distribution, %
Mill tailings, incl. pyrrhotite	540	58.5
Smelter slag	11	1.2
Nickel-copper matte	44	4.8
Sulfuric acid production	200	21.7
Stack emissions	104	11.3
Copper concentrate, etc.	23	2.5

Particulate emissions from the Falconbridge smelter were also reduced by 80% when the fluidized-bed roasting–electric furnace process replaced the old sintering blast furnace process in 1978.

The Outokumpu flash smelting process is probably the most environmentally compatible of the current commercial nickel smelting processes because it permits the capture of virtually all the sulfur dioxide produced prior to the conversion step. The recovery of sulfur dioxide from the off-gas stream from Peirce-Smith converters is not generally feasible due to the low sulfur content of the off-gas and intermittent nature of the operation.

12.4.3.1 New Developments in Nickel Smelting

In contrast to the copper industry, in which a number of continuous smelting processes have been commercialized, there has been little interest in developing a process for nickel concentrates in which the primary smelting and converting steps are combined into a single continuous operation. One such process was proposed by QUENEAU and SCHUMANN in 1976 but has not been adopted commercially [59].

The major development in nickel smelting during the 1990s will be the modernization of

Inco's aging nickel-copper smelter at Copper Cliff, Ontario. Ontario Government regulatory measures to reduce acid rain require that Inco reduce its emissions of sulfur dioxide from 685×10^3 t/a in 1990 to 265×10^3 t/a by 1994, corresponding to an increase in the fixation of the sulfur in the ore from 70% to 90%. In the existing operation, 55% of the sulfur is rejected to tailings as pyrrhotite, and a further 15% is converted either to acid or to liquid sulfur dioxide. The remaining 30% is emitted to the environment as low sulfur dioxide content off-gases from the Herreschoff roasters, reverberatory furnaces, and the nickel matte and copper converters.

Several potential smelting options were examined by Inco, including the roast-reduction-smelting process, which was tested on a plant scale at Thompson in 1979 [32], and the oxygen flash smelting of nickel concentrate, which was tested with the copper flash furnace at Copper Cliff in 1976 [60]. However, none of these options was acceptable since they did not eliminate the copper converting operation, which itself produces more than the 1994 sulfur dioxide emission limit of 265 000 t/a [61].

The strategy eventually selected for the modernization is based on the oxygen flash smelting of bulk nickel copper concentrate followed by converting the high-grade furnace matte in the existing nickel converters. The converter matte will be separated into metallics, nickel sulfide, and copper sulfide fractions using the existing matte separation process, and the iron-free copper sulfide (Cu_2S) will be oxygen flash smelted to semi-blister copper. In this way the weak gas streams from the roasters, reverberatory furnaces, and copper converters will be totally eliminated, and the volume of gases from the nickel converters will be halved. All the sulfur dioxide in the high-strength (80% SO_2) off-gas streams from the flash furnaces will be fixed as sulfuric acid or liquid sulfur dioxide. The oxygen flash smelting process is very energy efficient, and energy consumption in the smelter will be halved.

Since the entire nickel-copper separation will in future be carried out in the matte separation plant, Inco's milling operations will be simplified. Operations will be consolidated in the Clarabelle mill, and the Copper Cliff and Frood-Stobie mills will be closed. The function of the modernized Clarabelle mill will be to reject pyrrhotite and produce a bulk nickel-copper concentrate. A large new semiautogenous grinding mill and new flotation cells, more than ten times larger than the existing cells, will be installed. These changes are projected to increase the rejection of sulfur from the ore as pyrrhotite to tailings to 67% [61].

In the smelter, two large new flash smelting furnaces, each capable of treating 1800 t/d of bulk concentrate, and a smaller flash furnace capable of treating 725 t/d of Cu_2S concentrate, will be constructed. A new oxygen plant will produce 450 t/d to supplement the 1300 t/d currently available.

A new sulfuric acid plant with a design rate of 2300 t/d will handle the off-gas from both large flash furnaces. Off-gas from the copper flash furnace will form the feed to the existing liquid sulfur dioxide plant. Installation of the new acid plant will permit the closing of the roaster operation and acid plant at the iron ore recovery plant.

The first large flash furnace together with the new oxygen plant and acid plant are scheduled for completion in 1992, while the second large flash furnace will be operating by the end of 1993.

12.4.4 Treatment of Converter Matte

Nickel-copper converter matte is essentially a melt of nickel, copper, and sulfur with small amounts of cobalt, iron, and oxygen, and traces of the noble metals and various undesirable impurities, including selenium, tellurium, and entrained slag. In the South African platinum industry, where nickel copper mattes containing over 1000 g/t platinum group metals are common, the noble metal content of the matte far exceeds the base metal content in value. The platinum group metal contents of

the Sudbury mattes, although much lower than in the South African mattes, are still of major economic significance.

Further processing of nickel copper converter mattes is carried out to separate and recover nickel, copper, cobalt, and the noble metals. Mattes may be treated by hydrometallurgy (the Sherritt, Outokumpu, and Falconbridge leach processes), by electrometallurgy if they are low in copper (Inco's direct electrorefining of matte anodes), or by pyrometallurgy (Inco's slow-cooling matte separation process).

12.4.4.1 INCO Matte Separation Process

The controlled slow-cooling matte separation process [1] was developed by Inco in the 1940s to replace the obsolete Orford Process which depended on the different solubilities of copper and nickel sulfides in molten sodium sulfide. Other operations which had used the Orford Process, Rustenburg Platinum in the Republic of South Africa and the major Soviet nickel producers, have subsequently adopted the slow-cooling technique.

This process is based on the fact that when molten nickel-copper mattes freeze slowly, the constituents segregate into grains that are separate and distinct chemical phases. The major phases are Cu_2S and Ni_3S_2 , but if the matte contains less sulfur than is required to form these compounds, the excess nickel forms a magnetic alloy phase with copper, which also preferentially collects the noble metals. The slow-cooled matte can then be comminuted and separated into nickel sulfide, copper sulfide, and nickel-copper alloy fractions by normal mineral beneficiation techniques. The nickel-copper alloy, which is separated magnetically, contains virtually all

the platinum group metal and gold values at a substantially increased grade compared to the converter matte.

In the Inco matte separation plant at Copper Cliff (Figure 12.6) [34] molten sulfur-deficient converter matte (50% Ni, 26% Cu, 0.5% Fe, 22% S) is poured into molds at 1000 °C and cooled slowly over a period of four days to about 200 °C. The solid matte is crushed and ground and is then separated into its components by magnetic separation and flotation. The copper sulfide concentrate (73% Cu, 5% Ni), which also contains most of the silver, selenium, and tellurium, is converted to blister copper in Inco's copper smelting circuit. The silver, selenium, and tellurium are recovered from the copper refinery anode slimes. The magnetic nickel copper alloy (65% Ni, 20% Cu) forms the major feedstock to Inco's Copper Cliff nickel refinery, where the nickel is refined by the pressure carbonyl process to high-grade nickel powder and pellets, and copper and the precious metals are recovered from the refining residue. The nickel sulfide concentrate (70% Ni, 0.6% Cu), which is essentially depleted in precious metals, forms the feed to the fluidized-bed roasting plant.

The three large sulfide nickel operations in the former Soviet Union at Pechenga, Monchegorsk, and Norilsk, all use similar slow-cooling matte separation processes, producing separate nickel and copper sulfide concentrates. Rustenburg Platinum in the Republic of South Africa uses the slow-cooling technique to separate a magnetic nickel-copper alloy with a high noble-metal content for processing to recover and refine the platinum group metals, but does not separate the nickel and copper sulfides. The bulk nickel-copper concentrate is treated by pressure hydrometallurgy to separate the nickel and copper.

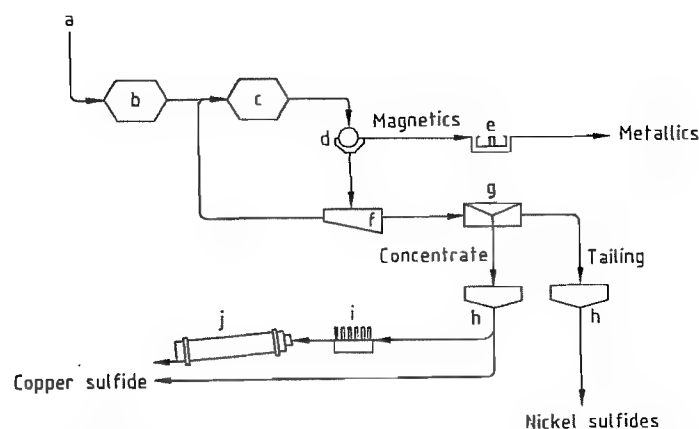


Figure 12.6: Flow sheet of the Inco matte separation process: a) Converter matte from Copper Cliff smelter; b) Rod mill; c) Ball mill; d) Magnetic separator; e) Centrifuge; f) Rake classifier; g) Flotation cell; h) Thickener; i) Disc filter; j) Dryer.

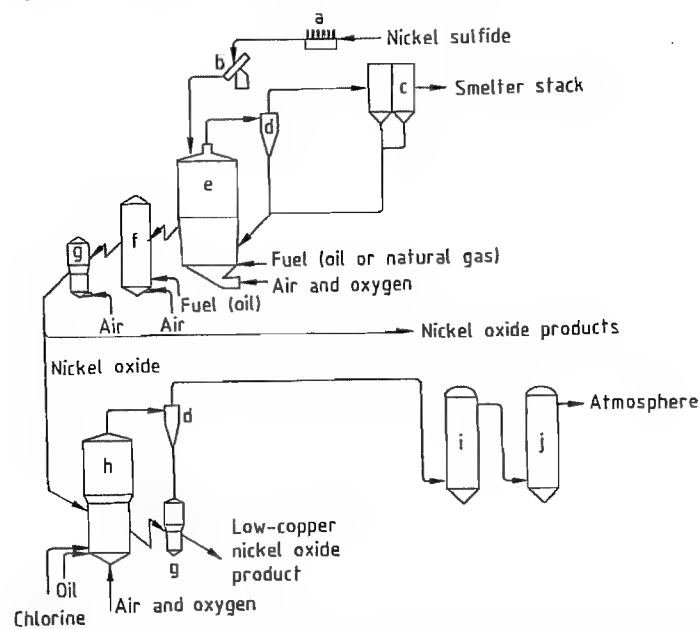


Figure 12.7: Flow sheet of the Inco nickel matte roasting process: a) Disc filter; b) Pelletizing disc; c) Electrostatic precipitator; d) Cyclone; e) Roaster; f) Reroaster; g) Cooler; h) Chlorination reactor; i) Splash tower; j) Packed tower.

12.4.4.2 Fluidized-Bed Roasting of Nickel Sulfide

Nickel sulfide concentrates are roasted in fluidized-bed roasters [62] to produce nickel oxide at Inco's matte treatment plant in Copper Cliff and at the major nickel operations in

the former Soviet Union. The dead roasting of finely ground nickel sulfide concentrates in a fluidized-bed roaster presents difficulties because nickel sulfide softens and becomes sticky at about 650 °C, while sulfur removal must be carried out at a temperature above 1100 °C, at which the sulfide is molten, to

achieve the required degree of sulfur elimination at an economic rate. A further problem is the very fine nature of the concentrates. Typically 99% of the particles are less than 75 µm, with about 20% in the 10 µm range. It is therefore difficult to feed such fine material into a fluidized-bed roaster without either incurring excessive dust carryover from the bed, or causing the bed to fuse with consequent loss of fluidization.

In Inco's practice (Figure 12.7) [34] the concentrate is pelletized in order to provide enough mass to carry the sulfide particles down through the rising gas stream into the bed. Agglomeration is carried out by adding recovered roaster dust (about 10% of the total) to the nickel sulfide concentrate slurry received from the matte flotation circuit. The green nickel sulfide pellets are charged into four fluidized-bed roasters which operate under optimum conditions at a superficial gas velocity of about 2 m/s with a bed expansion of about 150%. The average retention time of a particle in the bed is ca. 8 h. Roasting under these conditions is autogenous at 1100 °C, but the roaster air is enriched with oxygen to increase the elimination of sulfur and increase the concentrate throughput rate. A coarse granular nickel oxide (NiO) containing ca. 0.2% S is drawn off from the bed overflow. A single roaster can treat ca. 350 t/d of nickel concentrate.

The roaster calcine is either cooled in a fluidized cooler with water sprays from 1100 °C to 90 °C and shipped to one of Inco's nickel refineries (Copper Cliff or Port Colborne, Ontario; or Clydach, Wales), or is further desulfurized in a second fluidized-bed roaster. In this second roasting step the sulfur content is reduced to levels as low as 0.005%. This material is either marketed directly as 'Sinter 75' (75% Ni, 0.7% Cu, and 0.006% S), which is used in alloy steel making, or is treated by chlorination and reduction to lower its copper content. The removal of copper and other impurities is carried out by the injection of chlorine gas into a fluidized-bed reactor at 1200 °C, at a chlorine addition rate of about 3% of the reactor feed. The bed is heated by

light fuel oil and oxygen-enriched air. The reactor product typically contains 0.3% Cu and less than 0.01% S. It was formerly treated with a gas containing 75% hydrogen at 510 °C in another fluidized-bed reactor to yield Incomet, a metallic nickel product, which, however, is no longer made.

12.5 Hydrometallurgy of Nickel Concentrates and Mattes

Several hydrometallurgical processes [63] are in commercial operation for the treatment of nickel copper mattes to produce separate nickel and copper products. In addition, the hydrometallurgical process developed by Sherritt Gordon in the early 1950s for the direct treatment of nickel sulfide concentrates, as an alternative to smelting, is still commercially viable and competitive, despite very significant improvements in the economics and energy efficiency of nickel smelting technology [64].

In a typical hydrometallurgical process, the concentrate or matte is first leached in a sulfate or chloride solution to dissolve nickel, cobalt, and some of the copper, while the sulfide is oxidized to insoluble elemental sulfur or soluble sulfate. Frequently, leaching is carried out in a two-stage countercurrent system so that the matte can be used to partially purify the solution, for example, by precipitating copper by cementation. In this way a nickel copper matte can be treated in a two-stage leach process to produce a copper-free nickel sulfate or nickel chloride solution, and a leach residue enriched in copper. The copper-rich residue is treated by pressure leaching, or by roasting and leaching, to solubilize the copper as copper sulfate so that it can be recovered from solution electrolytically as cathode copper. Nickel is recovered from the purified nickel sulfate or chloride solution either electrolytically as a pure nickel cathode or by chemical reduction with hydrogen to give pure nickel powder.

Table 12.9: Hydrometallurgical nickel refineries [63].

Company/operation	Capacity, t/a Ni	Feed composition, %				
		Ni	Cu	Co	Fe	S
Falconbridge, Norway	54 000	35–40	30–35	1.0	2.5	22–24
Inco, Thompson	46 000	73	3	0.8	0.6	20
Western Mining	33 000	44–72	3–5	0.8	1–25	20–23
Sherritt Gordon	24 000	15–70	1–5	0.5	2–30	18–30
Sumitomo, Niihama	22 000	72	5	0.7	0.5	21
Rustenberg Refiners	20 000	47	27	0.5	3.0	21
Outokumpu, Harjavalta	17 000	55–65	25–35	0.6	0.2	6
SLN, Le Havre	16 000	75		1.5	2.5	20
Jianchuan, China	15 000	68	7	1.0	2.0	21
Bindura, Zimbabwe	14 400	66	25	0.6	0.2	6
Empress, Zimbabwe	5 000	40	52	0.2	0.2	6
Western Platinum	2 000	48	28	0.5	1.0	21

The range of compositions for mattes treated by hydrometallurgical processes is shown in Table 12.9 [63]. The nickel contents of the mattes treated hydrometallurgically are in the range 35–75 %, while the copper content varies from 0 to 52 %, and sulfur from 6 to 24 %. Low-copper mattes (< 10 % Cu) can be treated by ammoniacal pressure leaching, by ferric chloride leaching, or by direct electrorefining of the matte. High-copper mattes can be treated by high-pressure or atmospheric pressure sulfuric acid leaching or hydrochloric acid leaching.

The sulfur contents of the mattes are adjusted during the conversion process in the smelter to the optimal level for the subsequent leaching process. Sulfur levels are typically 20–23 %, except when the matte is to be treated by the Outokumpu atmospheric pressure sulfuric acid leaching process, for which the sulfur content is reduced to about 6 %.

12.5.1 Ammonia Pressure Leaching

The first successful commercialization of a hydrometallurgical process for the treatment of a nickel sulfide concentrate was realized by Sherritt Gordon Mines at Fort Saskatchewan, Alberta, Canada in 1954. This process was developed specifically to treat a pentlandite concentrate from Sherritt's Lynn Lake mine in northern Manitoba by ammonia pressure leaching [1, 65]. The original plant was de-

signed to produce 8000 t/a of nickel powder and briquettes by the chemical reduction of nickel in ammoniacal solution with hydrogen at high pressure. The same plant, with only minor process and equipment modifications, can now refine 24 000 t/a of nickel from a wide range of feed materials, including pentlandite concentrates, low-copper nickel mattes, and nickel sulfates and carbonates. The ammonia pressure leach process is also operated by Western Mining at Kwinana, Western Australia. Originally, this refinery processed nickel sulfide concentrates, but now treats a blend of converter and flash furnace nickel mattes to produce powder and briquettes at a rate of 33 000 t/a Ni. A block flow diagram of the ammonia pressure leach process as operated by Sherritt Gordon is shown in Figure 12.8.

The finely ground nickel sulfide concentrates and mattes are leached in ammoniacal ammonium sulfate solution at 80–95 °C under 850 kPa air pressure in a two-stage counter-current process in eight four-compartment horizontal autoclaves (Figure 12.9). Nickel, cobalt, and copper are dissolved as soluble ammonia complexes, while sulfide is oxidized to form a series of soluble thio salts. Reactive iron is oxidized and reports to the leach residue as a hydrated oxide together with pyrite which does not react in the leach:

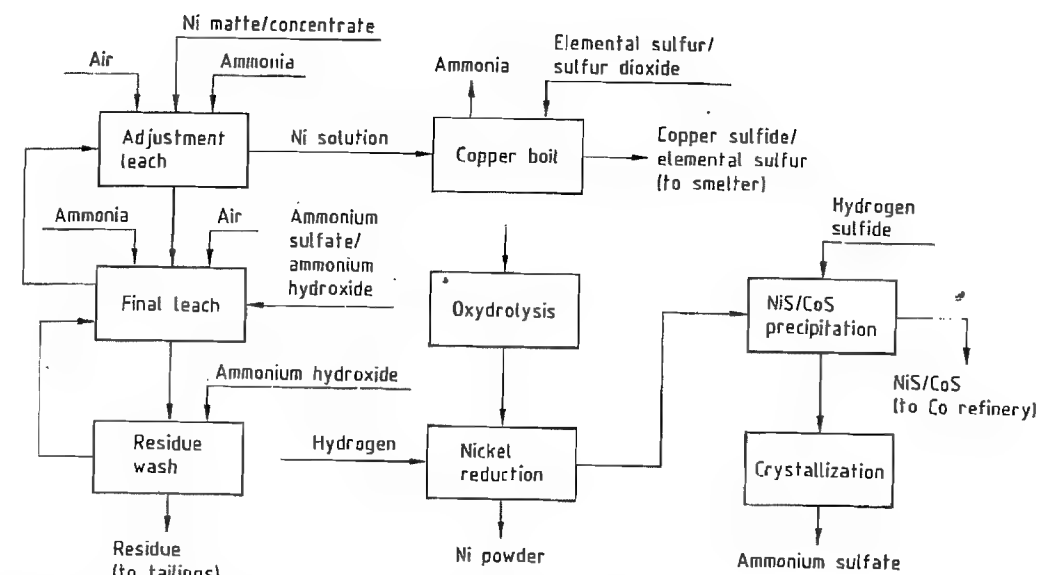
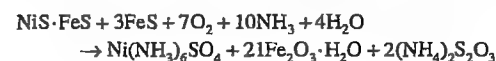


Figure 12.8: Flow sheet of the Sherritt ammonia pressure leach process.

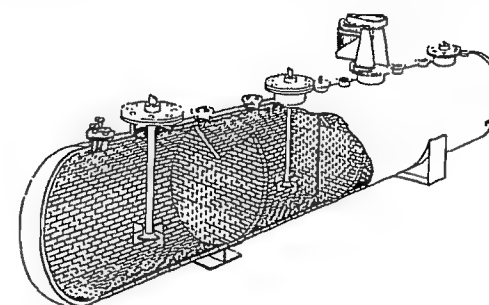
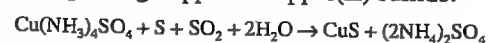


Figure 12.9: Cutaway view of a horizontal leaching autoclave.

The leach solution typically contains 50–60 g/L Ni, 1–2 g/L Co, 5–10 g/L Cu, 130 g/L NH_3 and varying amounts of thio salts, including thiosulfate and thionates, as well as ammonium sulfamate ($\text{H}_2\text{NSO}_3\text{NH}_4$), which is formed by the reaction of thionate with oxygen and ammonia.

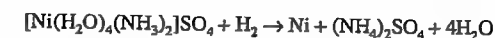
The leach solution is boiled to distil off the free ammonia, and elemental sulfur and sulfur dioxide are added to augment the thio salts in precipitating copper as copper(II) sulfide:



The copper sulfide is sold to a copper smelter. The ammonia to nickel molar ratio is

adjusted to 2:1 and the copper free ammoniacal nickel sulfate solution is oxidized at 235 °C under 4 MPa air pressure to convert the sulfur compounds to sulfate and to hydrolyze the sulfamate ion to sulfate. If these sulfur compounds were not fully converted to sulfate, the nickel powder product would contain unacceptably high levels of sulfur.

In the final step of the process, nickel is precipitated from solution as a metal powder by reduction with hydrogen under 3.6 MPa pressure at 200 °C in a four-agitator horizontal autoclave:

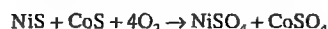


Details of the reduction technique are given in Section 12.6.4. The nickel powder is either compacted into briquettes for use in stainless steel production or is rolled into nickel strip for coinage production.

Under the specified process conditions cobalt is not precipitated during nickel reduction and the reduction end solution contains 1–2 g/L each of nickel and cobalt as well as about 400 g/L ammonium sulfate. This solution is treated with hydrogen sulfide to precipitate the nickel and cobalt as a mixed metal sulfide intermediate product, leaving a pure ammo-

mium sulfate solution which is evaporated to crystallize ammonium sulfate for sale as a fertilizer.

The mixed metal sulfides produced in both the Sherritt and the Western Mining nickel refineries are processed in Sherritt's cobalt refinery in Canada [65]. The sulfides are pressure leached in sulfuric acid under 1.15 MPa air pressure at 150 °C in a lead- and brick-lined, six-compartment horizontal autoclave to form a solution of nickel and cobalt sulfates:



Iron is removed from solution in a second autoclave by adjusting the pH to 2.5 with aqueous ammonia solution. At this stage the solution typically contains 40 g/L Ni, 30 g/L Co, and less than 10 mg/L Cu and Fe. The solution is then treated with aqueous ammonia solution under air pressure to oxidize the cobalt(II) ion to the cobalt(III) state which is stable as the soluble cobalt(III) pentammine complex ion $[\text{Co}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}]^{3+}$. Nickel is removed in a two-stage process by adding sulfuric acid to selectively precipitate nickel(II) ammonium sulfate, which is recycled to the nickel refinery. The cobalt/nickel ratio in the purified solution is typically 3000:1.

The cobalt(III) ion is reduced to cobalt(II) by treating the purified solution with cobalt powder and sulfuric acid. Cobalt powder is precipitated from solution by reduction with hydrogen at 180 °C and 4.3 MPa.

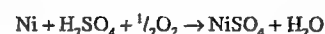
The pentammine cobalt refining process has also been operated by Outokumpu at Kokkola in Finland since 1968.

12.5.2 Atmospheric Acid Leaching

The atmospheric acid leach process for the treatment of high-copper, low-sulfur nickel matte was developed by Outokumpu [1] in 1960 to process material from its nickel mine in Finland, and was later adopted by the Bindura and Empress nickel refineries in Zimbabwe [66]. In this process the leaching operations are carried out in trains of air-agi-

tated pachuca tanks, in contrast to the mechanically-agitated horizontal autoclaves used in the pressure leaching process.

The Outokumpu process is outlined in Figure 12.10. Granulated matte, typically analyzing 55–65% Ni, 25–35% Cu, 0.6% Co, 0.2% Fe, and 6% S, is ground to 90% less than 54 µm and leached at 80 °C in acidic sulfate solution in a three-stage countercurrent leach circuit. Nickel, which is largely present in the low-sulfur matte as metallic nickel, dissolves in the first stage leach by reaction with sulfuric acid and with soluble copper, which is cemented from solution as copper metal. Copper sulfide in the matte does not react:



Most of the remaining nickel and some of the copper is leached in the second and third leach stages, which operate under increasingly oxidizing and acidic conditions. The solution from the first leach stage is a copper-free nickel sulfate solution, while the residue from the third stage is enriched in copper relative to nickel. Metal extractions in the atmospheric leach are typically about 90% Ni and 50% Cu.

The atmospheric leach residue, which contains about 15% Ni, 50% Cu, and 20% S, was originally recycled to the Outokumpu nickel smelter to recover the metal values. This residue is now treated in a fourth stage, a pressure leach under mildly oxidizing conditions at 160 °C, in which the nickel is extracted selectively, leaving a low-nickel, high-copper sulfide residue that can be treated directly in the copper smelter [67].

The Bindura and Empress refineries do not have a pressure leaching step and operate in the original Outokumpu mode, with copper recovery by electrowinning from the second-stage leach liquor, and recycle of the leach residue to a nickel smelter. At the Empress refinery, good quality copper cathode is produced, despite an unfavorable copper to nickel ratio in the solution, by using air-sparged cells at relatively low current density [66].

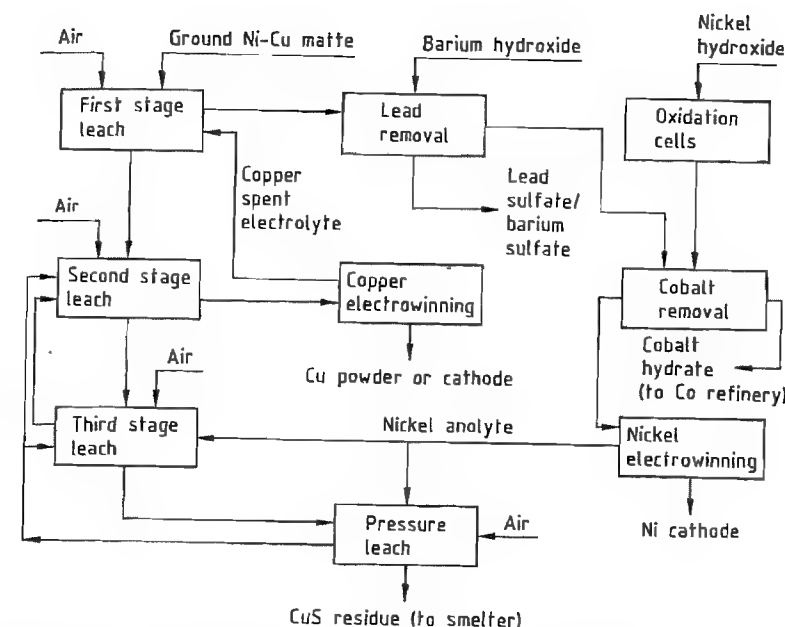
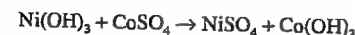


Figure 12.10: Flow sheet of the Outokumpu atmospheric acid leach process.

The first stage atmospheric leach step is primarily a solution purification step designed to produce a copper-free nickel sulfate solution. Air addition rates are reduced in the later pachuca leach tanks in the first stage to avoid redissolution of copper, and the pH is allowed to rise to 6.0 to ensure precipitation of iron by hydrolysis. Lead is precipitated by adding barium hydroxide or carbonate to the solution, either in the first stage leach or in a separate process step, to precipitate lead sulfate, which coprecipitates with barium sulfate. Cobalt is separated from the nickel sulfate solution in a later step, in which a slurry of nickel(III) hydroxide is added to precipitate cobalt as cobalt(III) hydroxide:



The nickel(III) hydroxide is produced by electrolytic oxidation of nickel(II) hydroxide, formed by neutralizing purified nickel sulfate solution with sodium hydroxide. The cobalt(III) hydroxide precipitate is refined to cobalt metal and cobalt salts by the pentammine process at Outokumpu's cobalt refinery at Kokkola, Finland.

Nickel is recovered from the purified nickel sulfate solution, which contains about 75 g/L Ni, as a high-grade cathode by direct electrowinning (see Section 12.6.2). Anolyte solution containing about 50 g/L Ni and 50 g/L H_2SO_4 , is recycled for use as a leachant in the leaching circuits.

12.5.3 Acid Pressure Leaching

The acid pressure leaching process for the treatment of high-copper nickel mattes was developed by Sherritt Gordon during the 1960s and is currently operated by all four platinum producers in the Republic of South Africa: Rustenburg Refiners, Impala Platinum, Western Platinum, and Barplats [68, 69]. A similar process was also operated by the Amax nickel refinery in Louisiana, United States, from 1974 to 1986 [70, 71].

Acid pressure leaching is normally carried out in brick- and lead-lined horizontal multi-compartment autoclaves at 135–160 °C and oxygen partial pressures of 140–350 kPa. The major advantage of this process for the platinum producers is that very high extractions of

nickel, copper, and sulfur can be achieved. Typically, the metal and sulfur extractions are greater than 99.9%, so that the leach residue is a high-grade platinum group metal concentrate that is virtually free from nickel, copper, and sulfur and can be treated directly in a platinum refinery. An upgrading factor for the platinum group metals of over 100 from the matte to the leach residue is readily attainable [69].

The process flow sheet differs significantly for the various operations. Rustenburg and Impala use two countercurrent stages of continuous pressure leaching at 135–150 °C, while the smaller Western Platinum and Barplats refineries operate an atmospheric leach at 85 °C followed by a single-stage continuous pressure leach at 160 °C. The nickel products also differ widely. Rustenburg Refiners recover nickel as a high-purity cathode by direct electro-winning, whereas Impala produces nickel powder and briquettes by hydrogen reduction, and Western Platinum and Barplats produce crystalline nickel sulfate, which is processed to metal or plating salts elsewhere.

The Impala Platinum flow sheet [72] is outlined in Figure 12.11. The nickel copper matte

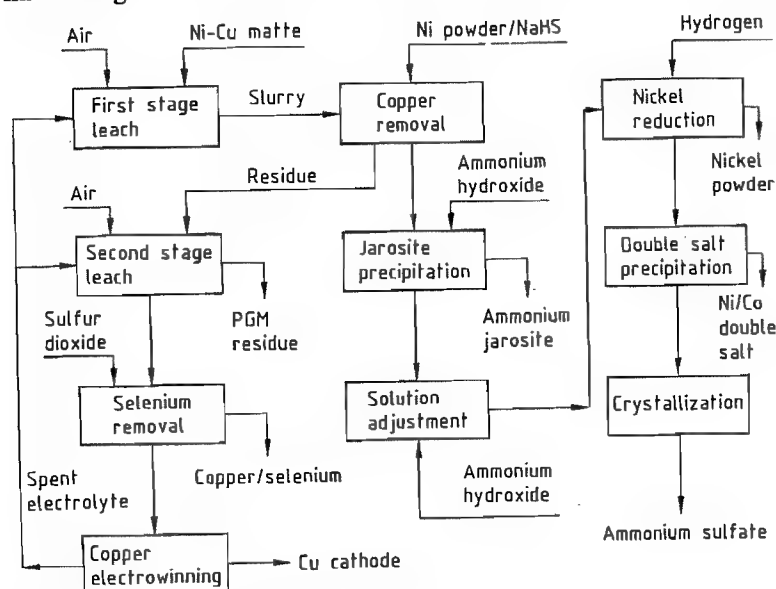
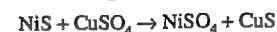
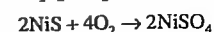
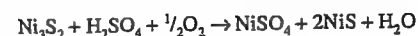
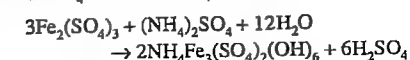
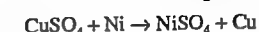


Figure 12.11: Flow sheet of Impala Platinum acid pressure leach process.

is leached in two stages at 135 °C under 1 MPa air pressure in spent copper electrolyte solution.



Solution from the first stage leach, which contains a high concentration of nickel (typically 100 g/L Ni) and low levels of copper and iron, is contacted with nickel powder and sodium hydrosulfide to precipitate copper, and iron is then removed as an ammonium jarosite precipitate using a horizontal multicompart-ment autoclave operating at 150 °C:



The jarosite precipitation step also effectively removes lead and arsenic from the nickel sulfate solution. The purified nickel sulfate solution is adjusted with aqueous ammonia solution to form the nickel(II) diamine complex ion, and nickel is recovered as a powder by reduction with hydrogen under pressure:

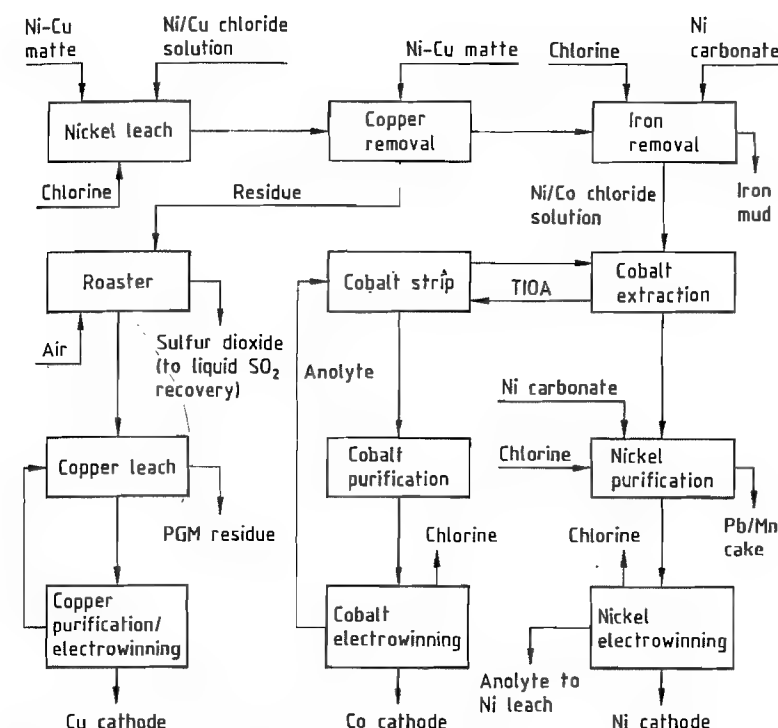
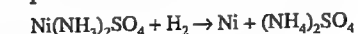
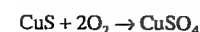
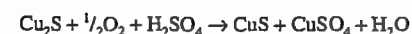
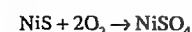


Figure 12.12: Flow sheet of the Falconbridge refinery process.

Cobalt and residual nickel are recovered from the reduction end solution as the nickel sulfate cobalt sulfate ammonium sulfate double salts, which are refined to produce cobalt metal powder by the Sherritt pentammine process and hydrogen reduction. The residue from the first stage leach is leached under more oxidizing and more acidic conditions in copper spent electrolyte in the second-stage pressure leach, which completes the extraction of nickel and copper sulfides:



The solution from the second-stage pressure leach, which contains both nickel and copper sulfate with traces of iron and selenium, is treated with sulfur dioxide to precipitate selenium as copper(I) selenide, and copper is recovered as cathode by electro-winning. The spent electrolyte, which contains

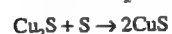
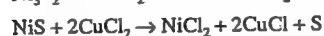
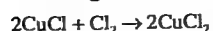
high levels of nickel as well as 20 g/L Cu and 50–70 g/L H_2SO_4 , is recycled to the pressure leach circuits. The second-stage leach contains the platinum group metals, with only minor levels of nickel, copper, and sulfur.

12.5.4 Chloride Leach Processes

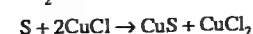
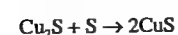
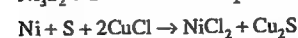
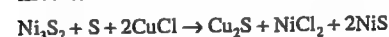
Nickel matte refining processes based on leaching in chloride solution in the presence of chlorine gas have been developed and successfully commercialized by Falconbridge at Kristiansand in Norway [73] and by Société Le Nickel (SLN) at Le Havre-Sandouville in France [74]. Leaching of the matte is carried out at atmospheric pressure at the boiling point of the leach solution (ca. 110 °C). Chlorine, which is recovered from the electrolysis cells, is sparged directly into the leach tanks. In the SLN process the leachant is the iron(III) chloride solution recovered from an iron removal step, whereas in the Falconbridge process the leachant is a solution of copper and

nickel chlorides recycled from the copper residue treatment circuit. The flow sheet of the Falconbridge process is shown in Figure 12.12.

Granulated nickel copper mattes from the Falconbridge smelter in Ontario, Canada and from BCL in Botswana, with an average composition of 40–45% Ni, 25–30% Cu, 20–22% S, 2–3% Fe, and 1–1.5% CO, are ground in a ball mill [73]. The ground matte is leached with chlorine in a nickel copper chloride solution in a train of agitated tanks. The leaching conditions are controlled by means of redox potential measurements to ensure selective leaching of nickel:



Essentially all the copper and sulfur present in the matte remain in the leach residue as CuS. The leach residue still contains about 8% Ni as unreacted NiS, and the leach solution still contains high concentrations of copper. The leach slurry is therefore heated to 140–145 °C in two vertical autoclaves, connected in series, to promote the precipitation of copper and the dissolution of nickel by a series of metathesis reactions:



The discharge from the autoclaves, which still contains about 7 g/L Cu in solution, is treated with fresh matte to reduce the copper concentration to less than 0.5 g/L. Overall nickel extraction is about 90%, and the final residue contains 6–8% Ni.

Iron, which is largely dissolved in the chlorine leach, is precipitated by oxidation with chlorine and hydrolysis with nickel carbonate. Cobalt is extracted from the nickel chloride solution by solvent extraction with triisooctylamine (TIOA) and, after purification of the strip solution, is recovered as high-purity cathode by electrowinning. The nickel

chloride raffinate is diluted and purified further by treatment with chlorine and nickel carbonate to remove the remaining traces of cobalt, iron, copper, arsenic, lead, and manganese. High-purity nickel is recovered by direct electrowinning as cathode, and as crowns by direct plating onto a suitably masked blank.

Copper is extracted from the chlorine leach residue by roasting it in a fluidized-bed roaster to convert the copper sulfide and elemental sulfur to copper oxide and sulfur dioxide, which is converted to sulfuric acid, and leaching the calcine in sulfuric acid to selectively leach the copper. The copper is recovered from the sulfate solution by conventional electrowinning.

The calcine leach residue, which contains 50% Ni and 18% Cu as well as the platinum group metals (PGM), undergoes further chloride leaching to recover the nickel and copper in solution for recycling to the leach circuit, leaving the platinum group metals in an upgraded concentrate. Typical process stream compositions for the Falconbridge operation are shown in Table 12.10.

Table 12.10: Process data for the Falconbridge chlorine leach process [73].

Stream	Ni	Co	Cu	Fe	S	Cl
Matte, %	45	1	28	2	22	
Feed solution, g/L	60		25	1		90
Sulfide leach residue, %	7	0.5	56	2	33	0.3
Pregnant solution, g/L	230	5	0.5	6		270
Ni electrolyte, g/L	60					60
Roaster calcine	9	0.5	63	2	0.5	
Cu electrolyte, g/L	60	6	60	2.5		
PGM concentrate, %	20	1	25	5	15	5

In the SLN process, in which the feed matte produced from laterite ore in New Caledonia contains virtually no copper, the pregnant leach liquor contains 200 g/L Ni with 5 g/L Co and 10 g/L Fe. Iron is removed as ferric chloride by solvent extraction with tributyl phosphate (TBP). Part of the ferric chloride strip solution is recycled to the chlorine leach, while the balance is concentrated and sold. Cobalt chloride is extracted with TIOA and sold as solution for cobalt recovery elsewhere.

Nickel is recovered from the purified solution as high-purity cathode by electrowinning [74].

12.5.5 Treatment of Nickeliferous Pyrrhotite [1]

Large tonnages of pyrrhotite concentrates containing up to 1% Ni are currently rejected in the milling and concentrating operations of the major Canadian nickel producers as a means of reducing the iron and sulfur inputs to their smelters, and hence reducing sulfur dioxide emissions. These pyrrhotite concentrates represent a major potential source of nickel and several attempts have been made to develop economically viable processes to exploit them. The primary requirement for a pyrrhotite treatment process is that it should produce an iron ore suitable for use in the steel industry and yield a good recovery of nickel. Such processes are typically based on roasting to eliminate all or part of the sulfur and hydrometallurgical treatment of the calcine to recover the nickel.

In 1956 Inco commissioned a plant at Copper Cliff, Ontario, to treat 1.2×10^6 t/a of pyrrhotite concentrate analyzing 0.9% Ni, 58% Fe, and 35% S. The iron sulfide concentrate was first oxidized to a low-sulfur calcine in fluidized-bed roasters, producing an off-gas containing sulfur dioxide from which sulfuric acid was produced. The calcine was then passed through a reducing kiln to reduce the nickel, cobalt, and copper oxides selectively to metallic form, so that they could be dissolved selectively in ammoniacal ammonium carbonate solution. The solution was purified to remove copper as the sulfide and nickel was precipitated as a basic nickel carbonate. The basic carbonate was calcined to a marketable oxide product containing 77% Ni. The leached iron oxide residue was pelletized and indurated for market. This plant operated until the early 1980s, when marginal economics and increasing constraints on sulfur emissions resulted in its closure.

From 1960 until the early 1970s, Falconbridge operated a process in which pyrrhotite concentrate, analyzing 1.1% Ni, 57% Fe, and

360% S, was sulfation roasted at 680 °C to convert the nickel, copper, and cobalt to their water-soluble sulfates. The calcine was then water-leached to extract the metals, and nickel, cobalt, and copper were precipitated from solution by cementation on iron turnings for recycling to the smelter. The iron oxide product analyzed 66% Fe, 0.13% Ni, and 0.5% S.

12.6 Refining [1, 63]

Nickel differs from copper in that it is largely used as an alloying element in stainless steel and alloy steel production. Thus, whereas most copper is used in electrical and thermal energy applications, which require a highly refined metal, a high-purity metal is not required for many of nickel's most important markets. Nickel products such as nickel oxide, metalized nickel oxide, and ferronickel, which are designated Class II products, are produced directly by smelting and roasting and are sufficiently pure, without refining, for many nickel applications such as stainless steel production. These Class II products may contain significant levels of cobalt and copper and a range of trace impurities.

In other applications, high-purity nickel is essential and Class I nickel products, which include electrolytic cathode, carbonyl powder, and hydrogen-reduced powder, are made by a variety of refining processes. In general nickel is refined to decrease to an acceptable level only those impurities which would have an adverse effect on subsequent processing or on the properties of the refined metal product. These elements include antimony, arsenic, bismuth, cobalt, copper, iron, lead, phosphorus, sulfur, tin, and zinc. Cobalt, which resembles nickel closely in physical and chemical properties, is difficult to remove completely and since it is not often a serious contaminant in most applications for nickel, many Class I products contain quite high levels of cobalt.

The object of the refining process is not only to remove the impurities from the nickel, but also to recover those that have an economic value. Obvious examples are the pre-

cious and platinum group metals (Pt, Pd, Os, Rh, Ir, and Ru), cobalt, and copper; sulfur, selenium, and tellurium can sometimes also be recovered economically. Historically the first successful nickel refining operation was established by the Mond Nickel Company (later absorbed by Inco) at Clydach, Wales, in 1902, using the carbonyl refining process invented by LUDWIG MOND and CARL LANGE in 1889. This refinery is still in operation using a modern version of the carbonyl process. A large refinery that uses a high-pressure version of the carbonyl process was established by Inco at Copper Cliff, Ontario in 1972 [75].

The first electrolytic nickel refinery, treating nickel metal anodes, was built by Hybinette in Kristiansand, Norway, in 1910, and this plant was acquired by Falconbridge in 1928. The Kristiansand Refinery was modernized in the late 1970s by replacing the Hybinette process with the present chlorine leach process [73]. Inco established its first nickel refinery in Canada at Port Colborne, Ontario, in 1926, using a version of the Hybinette refining process. This refinery operated until 1984. In 1989 the only electrolytic nickel in North America was produced by Inco's refinery at Thompson, Manitoba, which electrorefines matte anodes [76]. This process is also operated in Japan [77] and China. The electrorefining of nickel metal anodes, which is effectively obsolete in Western Europe and North America, is still practiced in the former Soviet Union [44].

Outokumpu, SLN, and Falconbridge in Europe and Bindura, Empress, and Rustenburg Refiners in Southern Africa all recover electrolytic nickel by direct electrowinning from purified solutions produced by the leaching of nickel or nickel copper mattes. Sherritt Gordon in Canada, Western Mining in Australia, and Impala Platinum in the Republic of South Africa recover refined nickel powder from purified ammoniacal solution by reduction with hydrogen.

12.6.1 Electrorefining

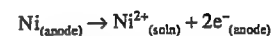
Nickel electrorefining [1] is carried out in a tank house containing a large number of electrolytic cells, each filled with a mixed nickel sulfate nickel chloride solution, and containing 30–40 anodes (slabs of metallic nickel or nickel matte), interspersed with cathodes that are thin sheets of pure nickel. The anodes and cathodes in each cell are connected electrically in parallel, and the cells are connected in series. When electrical current is passed through the cells the anodes dissolve, and pure nickel deposits on the cathodes. Cathodes and anodes are replaced periodically to maintain continuity of production.

Crude nickel anodes are made by reducing nickel oxide with coke at temperatures up to 1540 °C and casting the molten metal in molds. The pure nickel starting sheets are made in special electrolytic cells in which nickel is deposited onto permanent stainless steel or titanium cathode blanks, from which the thin sheet is stripped after 24 or 48 h of deposition. The sheets are fitted with suspension loops and placed in the production cells. The electrolytic cells are normally made of concrete and are lined with an acid-resistant membrane such as glass fiber reinforced plastic material.

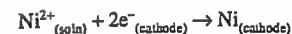
Nickel refining can be carried out with pure sulfate, mixed sulfate chloride, or pure chloride nickel electrolytes. In practice, the mixed sulfate chloride system is normally used for the electrorefining of either nickel metal or nickel matte. Sulfate and chloride electrolytes are used in the nickel electrowinning processes. The sulfate chloride electrolyte has two major advantages over the sulfate system, in having a higher conductivity which results in a lower cell voltage, and in permitting the use of chlorine for electrolyte purification.

12.6.1.1 Refining of Nickel Metal Anodes

In the refining of nickel metal anodes the principal reaction at the anode is the dissolution of nickel metal as nickel ions:



The principal cathodic reaction is the reduction of nickel ions from solution:



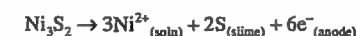
At the normal cell operating voltage (ca. 1.6 V for metal anodes) the principal impurities from the anode such as iron, cobalt, lead, arsenic, and copper go into solution with the nickel. Silver, gold, the platinum group metals, sulfur, selenium, and tellurium fall to the bottom of the cell as an insoluble slime. If the soluble impurities reach the cathode surface they will codeposit with the nickel. Consequently, to avoid contamination of the refined nickel cathodes, the impure anolyte solution is taken through a purification process. The purified solution is then returned to the cathode compartment of the cell, which is segregated from the anode by a porous diaphragm in the form of a bag or box enclosing the cathode. The purified solution is fed into the cathode compartment at a rate sufficient to maintain the rate of nickel deposition. The diaphragm cloth is tightly woven so that a hydrostatic head of solution builds up relative to the rest of the electrolyte. This hydrostatic head forces nickel-depleted electrolyte through the diaphragm, from the cathode compartment into the anolyte, at a rate sufficient to prevent the ingress of either anolyte itself, or impurity ions, by diffusion into the cathode compartment.

12.6.1.2 Refining of Nickel Matte Anodes

Nickel sulfide anodes can be electrorefined directly to pure nickel cathode without the intermediate process steps of roasting the sulfide to oxide and reducing the oxide to produce metallic nickel anodes. Nickel sulfide anodes can be cast directly from low-copper converter matte or from melted nickel sulfide concentrate produced by the matte separation process. Controlled cooling is necessary to produce anodes with the required mechanical properties. The anodes consist essentially of Ni_3S_2 and nickel alloy, but can contain up to

3 % copper as Cu_2S and other impurities such as iron, cobalt, lead, zinc, arsenic, selenium, and platinum group metals. Control of the sulfur content of the anodes is important because at sulfur contents of less than 15 %, the metallic nickel alloy phase dissolves preferentially, leaving nickel sulfide in the slime. At sulfur contents above 15 %, the matte anodes corrode uniformly to yield a slime containing elemental sulfur.

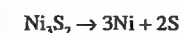
The principal anodic reactions are the oxidation of sulfide to elemental sulfur with simultaneous release of metal ions to the solution and of electrons to the anode:



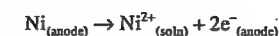
The cathodic reaction is the same as in the metal anode refining process:



The net cell reaction for the nickel sulfide phase is thus

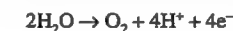


The metallic nickel phase dissolves electrolytically as in the refining of nickel metal anodes:



The actual cell voltage, including the potential drops across the contacts and through the electrolyte, is about 2.8 V for newly charged matte anodes. As the anodes corrode, the sludge, which consists mainly of elemental sulfur, forms a strongly adherent porous surface layer which causes an increase in volume and effectively doubles the bulk of the anode. As the sludge layer becomes thicker, the electrical resistance between the electrodes increases, and the cell voltage increases to about 4.0 V by the end of the anode cycle. The increase in cell resistance also results in increased heating of the electrolyte. The solution temperature rise in the cell increases from about 15 °C at the start of the anode cycle to about 25 °C at the end of the cycle.

The anode potential is sufficiently high that some water is decomposed:

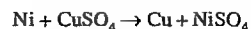


This unwanted reaction, together with the electrolytic dissolution of impurities from the anode, lowers the anode nickel dissolution efficiency so that nickel is removed from solution at the cathode faster than it dissolves at the anode. The imbalance is corrected during electrolyte purification by dissolving matte in the electrolyte to neutralize the free acid and replenish the nickel content.

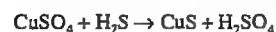
Operation of the nickel matte refining cell is similar to that of the metal anode cell except that the anodes are enclosed in bags to collect the voluminous sludge. The anode spacing in the matte refining cell is greater than in the metal refining cell, to allow for the increase in volume of the matte anode as it corrodes.

12.6.1.3 Solution Purification

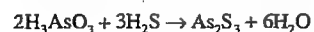
For the production of high-quality nickel cathode it is essential that the anolyte solution be purified before it is supplied to the cathode compartment. The purification methods used [1, 78] depend on the impurities present in the anode. Copper is often removed by cementation with activated metallic nickel powder, causing copper ions to precipitate as metallic copper while metallic nickel dissolves:



Alternatively copper may be precipitated as the sulfide with hydrogen sulfide:

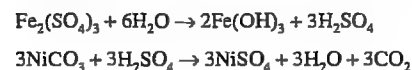


This procedure, which is used in the matte electrorefining process, also precipitates arsenic:



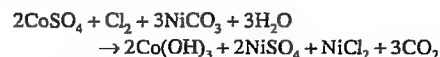
Careful control of the redox potential is necessary to ensure complete precipitation of copper and arsenic while minimizing the coprecipitation of nickel.

Iron is normally removed by treating the solution with chlorine and nickel carbonate to oxidize the iron to iron(III) and precipitate iron(III) hydroxide by hydrolysis:



Iron(III) hydroxide coprecipitates other impurities from the anolyte, particularly lead and arsenic. In the pure sulfate electrolyte systems, oxidation of iron is accomplished by using air instead of chlorine. Iron can be removed from pure chloride electrolytes by solvent extraction with tributyl phosphate.

Cobalt is precipitated as cobalt(III) hydroxide by treating the solution with chlorine or nickel(III) hydroxide to oxidize the cobalt(II) to cobalt(III). Nickel carbonate is added to control the pH.



Most of the cobalt precipitates at pH 4 at an oxidation potential of +1 V. Chlorine cannot be used in pure sulfate electrolyte, and in this system, nickel(III) hydroxide is normally used. Other oxidants which can be used to remove cobalt from the sulfate system include peroxide, persulfate, and ozone.

Cobalt is normally removed from pure chloride nickel electrolytes by solvent extraction with a tertiary amine such as triisooctylamine. Phosphine-based solvent extraction reagents such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) are used to extract cobalt from nickel sulfate solutions.

In practice the purified solutions used in nickel electrorefining are not simple mixtures of nickel sulfate and nickel chloride. The electrolyte is a weakly acidic aqueous solution of nickel, sulfate, sodium, and chloride ions, and boric acid. The sodium and chloride ions carry about 30% of the current through the electrolyte. Most of the remaining current is carried by the slower moving divalent nickel and sulfate ions, since the concentration of hydrogen ions is negligible. The boric acid, which exists largely as undissociated molecules, acts as a buffer to maintain the pH of the solution below 6. The presence of boric acid thus prevents the precipitation of nickel(II) hydroxide at the surface of the cathode by the reaction between nickel ions and hydroxide produced in the minor cathodic reaction involving the electrolytic decomposition of water.

12.6.1.4 Electrorefining Operations

Although it is not currently operated in North America or Western Europe, the refining of metallic nickel anodes is still practiced in the former Soviet Union. The Severonikel complex at Monchegorsk in the Kola peninsula has the capacity to produce 142 000 t/a of electrolytic nickel [44]. The Monchegorsk smelter treats a blend of high-grade nickel copper ores, concentrates, mattes, and scrap from the nickel mining operations at Norilsk and Pechenga. Separate nickel and copper sulfide concentrates are produced by the slow-cooling matte separation process. The nickel sulfide is dead roasted at 1170 °C with oxygen-enriched air (25% O₂), and the oxide calcine is reduced with coke in a rotary kiln to form a metallized oxide, which is melted at 1550 °C in an electric arc furnace for anode casting. About 3% of the metallized oxide powder from the reduction kiln is retained for use in electrolyte purification. The anodes typically weigh 350 kg and analyze (%): 86–88 Ni, 2 Co, 4.5 Fe, 4 Cu, and 0.2 S.

The anodes are refined in an electrolyte containing 75–78 g/L Ni, 130–150 g/L SO₄²⁻, 14 g/L Cl, and 6 g/L H₃BO₃, at pH 2. Each electrolytic cell contains 43 anodes and 42 cathodes, and operates at a current density of 250 A/m². The cathodes are enclosed in a synthetic fiber bag supported on a polypropylene frame. Starting sheets are produced by plating nickel on to titanium blanks for 24 h. The sheets are stripped manually. The anode cycle is 30 d, while the cathode cycle is four or six days. Anode slimes are recovered by washing adhering material off the corroded anodes, and from the bottom of the electrolytic cells, at the end of each anode cycle, for subsequent processing to recover precious metal values.

Impure anolyte solution is treated to remove iron, copper, and cobalt, and to replenish the nickel content of the electrolyte, before the purified solution is returned to the cathode compartments. Iron is removed by controlled oxidation with chlorine and neutralization with nickel carbonate. Copper is precipitated

by cementation on nickel powder from the reduction kiln, and cobalt is precipitated by oxidation with chlorine and hydrolysis with nickel carbonate under highly oxidizing conditions. The nickel content of the solution is replenished by pressure leaching nickel sulfide concentrate (Ni₃S₂) in sulfuric acid solution under 1 MPa air pressure in vertical titanium autoclaves.

The electrorefining of nickel sulfide anodes is carried out by Inco at its Thompson operation in Canada, by Sumitomo Metal Mining Company at Niihama in Japan, and at Jianchuan in China.

The Thompson smelter [76] produces sulfide anodes by casting molten converter matte (73% Ni, 0.8% Co, 2.5–3.0% Cu, 0.5% Fe, and 20% S) directly into anodes weighing ca. 240 kg. The cast anodes are cooled slowly over about 36 h to improve their mechanical handling characteristics, but are nevertheless more brittle than metal anodes and require careful handling.

The sulfide anodes are electrolyzed in diaphragm cells in a sulfate chloride electrolyte. Nickel, cobalt, and copper dissolve from the anode, while sulfur, selenium, and the noble metals form an insoluble sludge or slime, from which they can be recovered. Nickel is plated on to pure nickel starting sheets, made by manually stripping 24-h deposits from stainless steel blanks. The anode cycle is 15 d and the cathode cycle is 10 d. Plating is carried out at a current density of 240 A/m². Details of the tankhouse operating parameters are as follows [76]:

Capacity	45 000 t/a Ni
Cells	608
Cell dimensions	1.6 m × 0.9 m × 5.8 m
Cell construction	fiber reinforced plastic lined precast concrete
Anode weight	238 kg
Anode dimensions	1.1 m × 0.7 m × 63 mm
Anode spacing	210 mm
Anodes/cell	27
Anode cycle	15 d
Cathode dimensions	1.0 m × 0.7 m × 13 mm
Cathode weight	88.5 kg
Cathodes/cell	26
Cathode cycle	10 d
Electrolyte flow	0.64 m ³ /h per cell
Electrolyte temperature	50 °C

Current density 240 A/m²
Cell voltage 3-6 V

The anolyte purification circuits at Thompson remove copper and arsenic by precipitation with hydrogen sulfide. The nickel content of the electrolyte is then replenished by reacting the solution with ground matte anode scrap under oxidizing conditions. For every 100 kg of nickel plated out in the tankhouse only 87 kg dissolves from the anode. This discrepancy is caused by the dissolution of 4 kg of copper, 1 kg of cobalt, 0.5 kg each of iron and arsenic, and by the formation of 0.2 kg of hydrogen ions. In the final stage of purification cobalt and iron are oxidized and hydrolyzed by the addition of chlorine and nickel carbonate. The cobalt(III) hydroxide precipitate is worked up for cobalt recovery. The purified electrolyte typically contains 75 g/L Ni, 120 g/L SO₄²⁻, 28 g/L Na, 50 g/L Cl⁻, and 8 g/L boric acid.

Until 1984, the principal products of the Thompson refinery were full nickel cathodes and cut shapes, made by shearing cathodes grown on nickel starting sheets. Now about 40% of the refinery's production is "S" and "R" Rounds for the plating industry, which are made by plating nickel directly on to stainless steel blanks, covered by a heat-set epoxy mask, with circular areas of steel exposed to plating. Metallurgical data for the Thompson refinery, including the cathode nickel analysis, are given in Table 12.11.

Table 12.11: Metallurgical data for the Inco Thompson refinery [76].

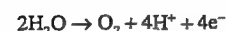
Element	Anode, %	Anolyte, g/L	Purified electrolyte, g/L	Electro-nickel, g/t
Ni	73		75	
Co	0.8	0.13	0.02	600
Cu	3.0	0.50	0.0007	25
As	0.2	0.03	0.0005	30
Fe	0.6	0.03		5
Pb	0.003			2
S	20			7

12.6.2 Electrowinning

Electrowinning differs from electrorefining in that it is used to recover nickel from a leach liquor and can therefore be carried out with an

insoluble anode, since the only function of the anode is to transfer electrons from the electrolyte to the external circuit. The electrowinning of nickel is practiced commercially with both pure sulfate and pure chloride electrolytes. In the sulfate system the anodes are made of chemical lead or antimonial lead, which have a relatively long life in sulfate solution, although soluble in chloride solutions. In the highly corrosive chloride system, dimensionally stable anodes, made by coating a titanium substrate with a platinum group metal oxide, are used.

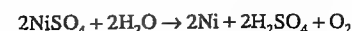
The principal anodic reaction in the sulfate system is the decomposition of water to produce gaseous oxygen:



The main cathodic reaction, as in electrorefining, is the deposition of nickel ions to form nickel atoms on the cathode:



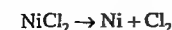
The overall cell reaction is:



The sulfuric acid generated at the anode is utilized by recirculating the anolyte to the leach circuits. In the chloride system the principal anodic reaction is the oxidation of chloride ion to chlorine gas:



The overall reaction is thus the decomposition of nickel(II) chloride to metallic nickel and chlorine gas:



The chlorine liberated at the anode is recycled for use in the leach circuits. In practice some decomposition of water also occurs to yield small quantities of hydrogen at the cathode and oxygen at the anode.

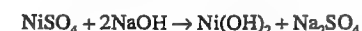
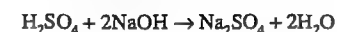
12.6.2.1 Electrowinning from Sulfate Electrolytes

In a sulfate electrowinning system the cathodes are suspended in bags, even though the nickel sulfate solution is purified before it enters the tankhouse. The cathode must still be

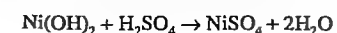
protected from the anolyte, which is strongly acidic due to anodic generation of hydrogen ions. A high concentration of hydrogen ions at the cathode would result in the formation of hydrogen gas which is formed in preference to nickel deposition, thus seriously reducing the current efficiency of the cell.

Details of the purification methods used to remove copper, iron, lead, and cobalt from nickel sulfate leach liquor prior to electrowinning are given in Section 12.5. Treatment of electrowinning anolyte or spent electrolyte varies depending on the type of leaching circuit used. In the Outokumpu atmospheric leach, in which very little sulfur is oxidized, almost all the anolyte can be recycled to the leaching circuits, where the acid is neutralized in leaching nickel from the matte, thus replenishing the nickel content of the solution. Only a small solution bleed is taken out of the circuit to control the concentration of sodium sulfate, which would otherwise build up to unacceptable levels.

In the Sherritt acid pressure leaching process, as practiced by Rustenburg Refiners, in which all the sulfur in the matte is oxidized to sulfate, a much larger bleed of solution is required to maintain a sulfur balance. Typically 25-35% of the anolyte stream must be removed from the circuit and treated to recover sodium sulfate. This bleed stream is reacted with sodium hydroxide or sodium carbonate to neutralize the acid and precipitate the remaining nickel as nickel(II) hydroxide or as basic nickel carbonate:



The nickel-free barren solution is evaporated to crystallize sodium sulfate. The precipitated nickel hydroxide or basic nickel carbonate is redissolved in a second portion of the anolyte stream to neutralize the acid content and replenish the nickel content:



This solution is recycled directly as feed solution to the electrowinning circuit. The balance of the anolyte is recycled for use in the

matte leach circuits, where the acid is neutralized and the nickel content replenished, and passes through the leach solution purification steps before returning to the tankhouse.

The Outokumpu nickel refinery at Harjavalta in Finland contains 126 electrowinning cells, each having 40 insoluble lead anodes and 39 cathodes [1, 48, 67]. The bagged cathodes are nickel starting sheets made by the deposition of nickel for 48 h onto a stainless steel mother blank. The deposits are stripped manually and automatically made up into starting sheets. The purified solution is fed to the cathode compartments at a rate sufficient to maintain a hydrostatic head of about 30 mm. The current density is 200 A/m², giving a cell voltage of about 3.6 V. The cathode cycle is seven days. The cells are hooded to collect and remove the oxygen and acid mist generated at the anode.

The feed solution at pH 3.2, containing 75 g/L Ni as well as sodium sulfate and boric acid, is heated to 60 °C and fed separately to each cathode compartment. The solution passes through the diaphragm cloth into the anolyte, which overflows from each end of the cell. The anolyte, which contains 50 g/L Ni and 40 g/L H₂SO₄, is recycled to the leaching circuits. The cathodes typically weigh ca. 75 kg and contain 99.95% Ni.

12.6.2.2 Electrowinning from Chloride Electrolytes

In the Falconbridge chloride electrowinning system [73], the dimensionally stable anodes are enclosed in a polyester diaphragm bag, to contain the chlorine gas generated in the anode reaction, and channel it to a vacuum hood fitted to the top of the anode. Ducts, connecting the top of the hood with a manifold that runs alongside the tank, allow the withdrawal of both chlorine and anolyte by suction. Purified solution is fed in at one end of the cell, and the solution level is held constant by maintaining a small overflow at the other end, while the greater portion of the electrolyte is withdrawn as anolyte with the chlorine gas.

The Falconbridge refinery at Kristiansand, Norway, which has a capacity of 54 000 t/a Ni, contains 326 electrolytic cells, of which 24 are devoted to starting sheet production. Each cell contains 46 anodes and 45 cathodes with an anode spacing of 145 mm. Typical operating parameters are as follows:

Inlet flow	4.0 m ³ /h per cell
Total current	24 000 A
Current density	220 A/m ²
Current efficiency	98–99%
Electrolyte temperature	60 °C
Catholyte Ni	60 g/L
Anolyte Ni	54 g/L

The refinery produces both regular nickel cathodes and Falconbridge crowns. The regular cathodes are produced by plating onto nickel starting sheets and are sheared to a variety of sizes for the nickel plating industry. Crowns weighing 30–60 g are produced by plating nickel onto specially designed cathode blanks, from which they are stripped and polished for market. The refinery produces a limited amount of exceptionally pure superelectro nickel, with less than 100 g/t of impurities including oxygen, and less than 5 g/t Co, by using a specially purified electrolyte.

12.6.3 Carbonyl Refining [1, 79, 80]

The reaction of carbon monoxide at atmospheric pressure with active nickel metal at 40–80 °C to form the gaseous nickel tetracarbonyl was discovered by LANGE and MOND in 1889 [75]. The reaction is readily reversible, with nickel tetracarbonyl decomposing to metallic nickel and carbon monoxide at 150–300 °C.

Nickel tetracarbonyl is a volatile liquid that melts at –19.3 °C and boils at 42.5 °C.

Under the mild conditions employed for reaction at atmospheric pressure, the carbonyl-forming impurities in crude nickel metal do not volatilize. Iron forms a volatile carbonyl, iron pentacarbonyl, Fe(CO)₅, with a freezing point of –20.5 °C and a boiling point of 103 °C, but the rate of formation is slow. Cobalt forms Co₂(CO)₈, which melts at 51 °C and decomposes at 52 °C to form Co₄(CO)₁₂, but both are solids with low volatility. Copper,

like most other elements, does not form carbonyls directly with carbon monoxide. Thus the extraction of nickel as a carbonyl from a crude metal feed is a highly selective process.

The formation of metal carbonyls by the interaction of carbon monoxide with reduced metals can be catalyzed. In fact if it were not for the large increase in reaction rate resulting from the addition of a controlled amount of catalyst, the tonnage extraction of nickel and iron as carbonyls from reduced metals would probably not be feasible. With the aid of catalysts or inhibitors it is possible to produce the carbonyls of nickel, cobalt, and iron either selectively or together.

Although catalysts such as ammonia, mercury, selenium, and tellurium have been used to increase the rate of nickel carbonyl formation, sulfide activation is normally used. Sulfur is a good, low cost catalyst which can be added in the form of hydrogen sulfide, carbonyl sulfide, or sulfur dioxide. It may be added during the reduction step or prior to volatilization. The carbonyl extraction process is notable not only for its selectivity in the volatilization of the metals as carbonyls but also for the relative ease with which the carbonyls can be separated and decomposed under mild conditions to produce high-purity metals. Nickel and iron carbonyls can be separated by simple fractional distillation as a result of the large difference in their boiling points.

The carbonyl process makes it possible to produce nickel of very high purity with an exceptionally low cobalt content, which makes it particularly useful for nuclear energy applications.

The thermal decomposition of nickel tetracarbonyl is carried out by two different methods. Very rapid heating of the gas phase produces a fine nickel powder. Alternatively if the carbonyl contacts a hot metal surface, nickel deposits on the surface. This effect is used to produce nickel granules by the successive deposition of layers of nickel onto a seed particle, until the required size is attained.

12.6.3.1 Atmospheric Pressure Carbonyl Process

The Inco nickel refinery at Clydach, Wales, began operation in 1902 using the Lange-Mond atmospheric pressure carbonyl process [1, 75]. Originally the plant treated nickel copper matte, but it now processes a granular nickel oxide, produced by fluidized-bed roasting of nickel sulfide at Inco's Copper Cliff smelter, which typically analyzes 74% Ni, 2.5% Cu, 1.0% CO, 0.3% Fe, and 0.1% S.

The refinery still uses the basic Lange-Mond process but the operation has been greatly increased in efficiency over the years. The first three steps in the process reduction, sulfide activation, and volatilization are now carried out in rotary kilns. The nickel oxide is first reduced to metal at 425 °C by countercurrent contact with preheated hydrogen gas. The metal is then sulfided in a smaller kiln to activate it, before being contacted countercurrently with carbon monoxide at 50–60 °C and atmospheric pressure in a third kiln. About 95% of the nickel volatilizes under these conditions but iron and cobalt are not carbonylated. The residue from the volatilizers is returned to Canada and forms part of the feed to the converters at the Copper Cliff nickel refinery.

The off-gas from the volatilizer kiln, which contains about 16 vol% nickel carbonyl, is fed to a pellet decomposer (Figure 12.13) where it is contacted with preheated nickel granules at 200 °C. The nickel carbonyl decomposes, releasing carbon monoxide and depositing a layer of metallic nickel on the granules, which steadily increase in size.

The decomposer is filled with about 30 t of pellets which flow downwards by gravity and are recirculated to the top of the vessel by an enclosed bucket elevator. As the pellets pass downwards they are heated to 200 °C before contacting the carbonyl-containing gas introduced at the bottom of the decomposer. The motion of the pellets prevents them from adhering together. Nickel powder is added periodically to nucleate new pellets, and market-size pellets (8 mm) are automatically segre-

gated from the smaller material and discharged. The off-gas from the decomposer contains ca. 93 vol% carbon monoxide and 0.1% nickel carbonyl, and is recycled to the volatilization kiln. Nickel pellets from the carbonyl process typically contain 99.97% Ni and less than 5 g/t Co. In addition to nickel pellets, carbonyl nickel powder is also produced at Clydach in electrically heated powder decomposers and accounts for ca. 20% of the refinery nickel output.

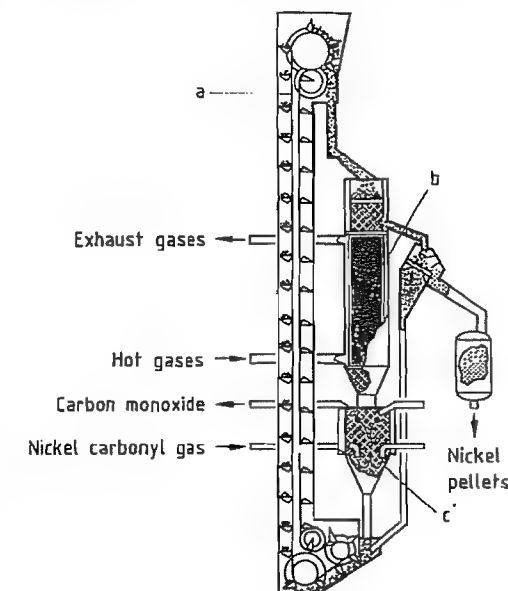
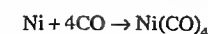


Figure 12.13: Cutaway view of a pellet decomposer: a) Bucket elevator; b) Preheater chamber; c) Reaction chamber.

12.6.3.2 High-Pressure Carbonyl Process (BASF)

Extraction of nickel with carbon monoxide is also used in processes that operate at high pressure and produce liquid nickel carbonyl. The volume change that occurs in the carbonyl reaction:



with four molecules of carbon monoxide forming one molecule of nickel carbonyl, means that an increase in pressure accelerates the formation of the carbonyl. The increased

pressure stabilizes the carbonyl and thus permits the process to be carried out at high temperature, which further increases the rate of reaction. As a result, activation of the nickel feed material is no longer necessary, and a wider range of feeds can be processed.

BASF in Germany operated a high-pressure carbonyl nickel refining process from 1932 until 1964. The feed materials were nickel copper matte or nickel scrap and residues. The feeds were melted and the composition was adjusted to provide just enough sulfur to combine with copper as Cu_2S and with part of the iron. The molten feed was granulated and reacted with carbon monoxide at 230 °C and 20 MPa. Over 95 % of the nickel was extracted as nickel carbonyl in a three-day batch treatment. Some iron was also carbonylated. Pure nickel powder was obtained by fractionation of the liquid carbonyls, and rapid heating of nickel carbonyl vapor to 280–300 °C.

12.6.3.3 Inco Pressure Carbonyl Process

The newest application of carbonyl refining to the treatment of a nickel-containing feed material is Inco's nickel refining complex in Copper Cliff, Ontario, which was commissioned in 1973 [80, 81]. This plant has a nominal capacity of 57 000 t/a of refined nickel.

The refinery consists of two operating plants: the converter plant and the pressure carbonyl plant. The converter plant produces granulated metallic nickel with a controlled sulfur content, using two top-blown rotary converters (TBRC's). The pressure carbonyl plant produces 45 000 t/a of nickel pellets, 9000 t/a of nickel powder, and 2200 t/a of ferromagnetic by-product from the granulated, sulfided nickel feed.

The principal feed materials supplied to the refinery by the Copper Cliff smelter are the metallics fraction from the matte separation process and the less pure portions of the nickel oxide made by roasting the nickel sulfide concentrate as well as various other nickel-bearing residues and intermediates. The novel feature of this process is the preparation of a

nickel feed material which could be carbonylated at moderate pressure without the need for a separate activation step.

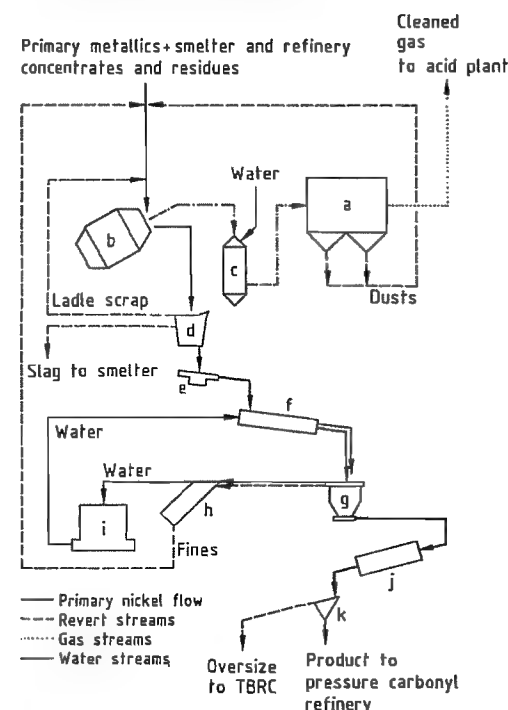


Figure 12.14: Flow sheet of the Inco pressure carbonyl converter plant: a) Electrostatic precipitator; b) Top-blown rotary converter (TBRC); c) Evaporation chamber; d) Bottom teeming ladle; e) Tundish; f) Granulating sluice; g) Dewatering bins; h) Lamella thickener; i) Cooling tower; j) Rotary dryer; k) Screen.

Figure 12.14 shows the process flow sheet for the preparation of the feed material in the converter plant. The feed materials are blended and smelted in two 50 t capacity top-blown rotary converters (Figure 12.15). Smelting is a batch operation carried out in three phases: charging/melting, blowing (sulfur removal), and reduction. In the charging/melting phase, blended feed materials are charged as the furnace rotates and is fired with a natural gas oxygen flame from a water-cooled lance. Coke is blended with the feed to reduce its oxide content, and the oxygen content of the flame is adjusted depending on the amount of sulfur to be removed. Charging is finished when the oxides have been reduced

and the temperature of the melt is about 1500 °C. During the charging and blowing phase the furnace is rotated to minimize dust emissions.

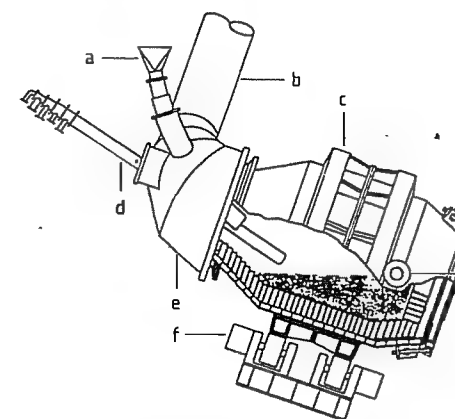


Figure 12.15: Cutaway view of a top-blown rotary converter: a) Water-cooled charging chute; b) Flue; c) Track ring; d) Water-cooled oxygen/natural gas lance; e) Hood; f) Rotate drive motor; g) Thrust roller.

In the blowing phase, a precalculated amount of high-pressure oxygen is blown at supersonic velocities into the converter charge to oxidize sufficient sulfur to produce a matte with a Cu/S ratio of about 4:1 (Cu_2S). In the reduction phase, oxides formed during blowing and oxygen dissolved in the bath are reduced with petroleum coke. Some sulfur removal also occurs when oxygen dissolved in the matte reacts with remaining sulfides. The converter is rotated at 15 rpm during reduction. Off-gases are drawn out through a movable hood and cleaned in electrostatic precipitators before being vented to a stack. The recovered dusts are recycled to a subsequent converter charge.

Molten matte at 1600 °C is granulated with high-pressure water jets at a rate of 1 t/min. The granulated matte is dried and transferred to the pressure carbonyl plant. The matte typically analyzes 75–80 % Ni, 12–17 % Cu, 2 % Co, 2 % Fe, and 3–4 % S, with a granule size of less than 9 mm.

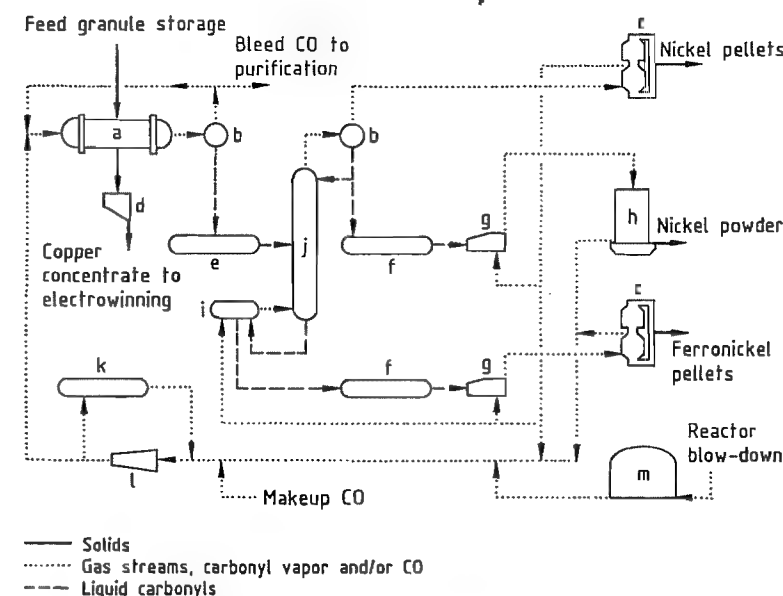


Figure 12.16: Flow sheet of the Inco pressure carbonyl refining process: a) Reactors; b) Condenser; c) Pellet decomposers; d) Slurry; e) Crude liquid storage; f) Storage; g) Vaporizer; h) Powder decomposers; i) Reboiler; j) Distillation columns; k) High-pressure CO storage; l) Main compressors; m) Low-pressure CO storage.

Figure 12.16 shows the process flow sheet for the pressure carbonyl refining operation. Matte granules are carbonylated in 150-t batches at temperatures up to 180 °C and pressures of 7 MPa in three horizontal cylindrical rotating reactors (Figure 12.17). Carbon monoxide is continually circulated through the reactor. Nickel carbonyl formation is very exothermic and the heat of reaction is removed by means of water-cooled heat exchanger tubes inside the reactors, which also serve as lifters to improve gas–solids contact as the vessel rotates. Micro-metallic filters at each end of the reactor prevent loss of solids entrained in the gas stream. The direction of gas flow is reversed periodically to prevent filter blinding.

Nickel and iron carbonyls are carried out of the reactor with the carbon monoxide stream, are liquefied by cooling, and stored as liquids at atmospheric pressure. The carbonylation reaction normally extracts about 97.5% of the nickel and 30% of the iron, leaving a residue typically containing 57% Cu, 8.5% Ni, 9% CO, 6% Fe, and 15% S, as well as the precious metals. The residue is treated hydrometallurgically to recover copper, cobalt, nickel, and the precious metals [82].

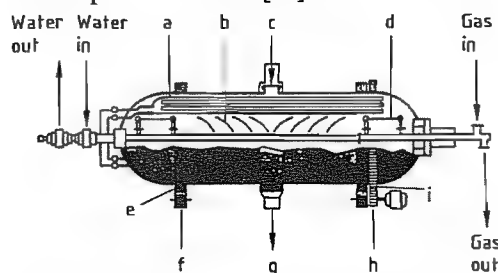


Figure 12.17: Cutaway view of a pressure carbonyl reactor: a) Coils; b) Flights; c) Feed chute; d) Metallic filters; e) Tires; f) Rollers; g) Discharge chute; h) Drive pinion; i) Spur gear.

The crude, liquid nickel–iron carbonyls typically contain 98.9% Ni and 1.1% Fe. This liquid is fractionated in two columns, each with twenty trays, to separate nickel carbonyl (*bp* 43 °C) from iron carbonyl (*bp* 103 °C). Distillation is carried out at below boiling temperatures with carbon monoxide as a carrier gas. Nickel carbonyl, which is obtained as

a mixture of vapor and liquid from the overhead partial condensers, is used to make extremely pure nickel powder and pellets. The bottoms from the reboilers, which contain 85% iron carbonyl and 15% nickel carbonyl liquids, are decomposed to form ferronickel pellets.

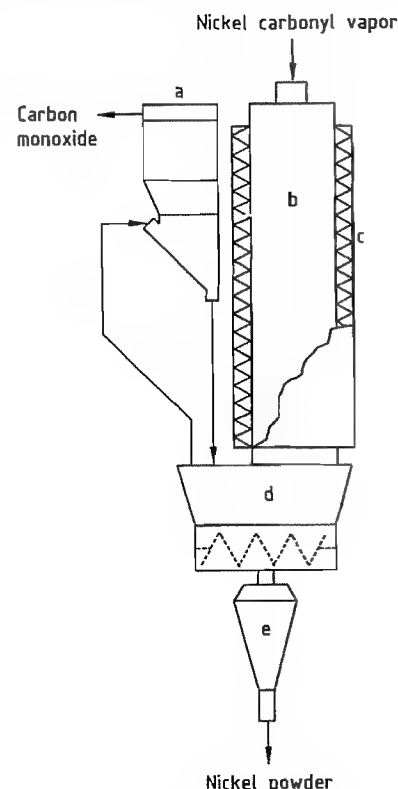
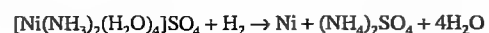


Figure 12.18: Cutaway view of a powder decomposer: a) Baghouse; b) Decomposer; c) Electric heaters; d) Connecting box; e) Discharge container.

The nickel carbonyl vapor from the distillation column passes directly to pellet decomposers (Figure 12.13) where it is contacted with preheated nickel pellets at 240–270 °C. The operation of the decomposers is essentially as described in Section 12.6.3.2 for the Inco refinery at Clydach. The condensed portion of the nickel carbonyl distillation overhead stream is revaporized with carbon monoxide carrier gas to avoid premature de-

composition and passed to electrically heated powder decomposers (Figure 12.18). Decomposition by thermal shock at 300 °C produces pure nickel powder, which can be varied in shape, size, morphology, and density by adjusting the operating conditions.

The iron carbonyl-containing bottoms product from distillation is treated by revaporizing the liquid at a sub-boiling temperature with carbon monoxide as carrier gas, and feeding it to a pellet decomposer to produce ferronickel pellets.

The pure nickel pellets, with a typical diameter of 10 mm, analyze over 99.97% Ni with 60 g/t C, 40 g/t O₂, and less than 0.2 g/t Co. The nickel powder, with a particle size in the range 3–7 μm, has significantly higher carbon and oxygen contents (650 g/t C and 570 g/t O₂).

12.6.4 Hydrogen Reduction to Nickel Powder

Nickel is recovered as a pure metal powder from nickel sulfate leach solutions by chemical reduction with hydrogen under pressure in several hydrometallurgical nickel refineries [1, 65]. Precipitation of the metal is carried out with an ammoniacal nickel sulfate solution having a molar ratio of ammonia to nickel of 2:1, so that the acid generated in the reduction reaction is neutralized by reaction with ammonia to form ammonium sulfate:

The reduction process is operated at 200 °C at a hydrogen pressure of 3 MPa in horizontal single-compartment autoclaves, each equipped with four agitators. The solution is processed batchwise, with the powder particles growing as successive layers of nickel are reduced, onto seed particles, from up to sixty batches of nickel-bearing feed solution. After each reduction or densification, which takes up to thirty minutes, the powder is allowed to settle, and the depleted solution is decanted off and replaced by fresh feed solution.

The nickel precipitation reaction can occur on any metal surface, and in the absence of suitable seed particles most of the metal deposition occurs on the vessel walls as a solid

plate. When suitable seed particles such as fine nickel powder are available, most of the nickel deposits on these particles, but even so, a minor but significant amount of nickel still plates on the walls, and must be released periodically. Normally this plating leach is carried out after each cycle of 50–60 densifications, and the leach liquor produced is used to prepare the seed particles for the subsequent densification cycle.

Seed particles are produced by adding an aqueous solution of iron(II) sulfate to the plating leach liquor to form a finely divided precipitate of ferrous hydroxide, and applying a hydrogen overpressure of 2.5 MPa at 115 °C. Under these conditions the nickel deposits onto the nuclei of ferrous hydroxide to form very fine particles of nickel metal, which provide the seed particles for densification. Once the nickel seed particles are formed, subsequent nickel deposition occurs autocatalytically on the surface of the particles, in preference to the vessel walls.

The reduction reaction is selective for nickel from a solution containing 50 g/L Ni and 1 g/L Co until the nickel content drops to about 1 g/L. Reduction is normally stopped at this point, leaving a solution containing about 1 g/L Ni and 1 g/L Co. This solution is reacted with hydrogen sulfide to precipitate a mixed nickel cobalt sulfide, which is treated hydrometallurgically to recover reformed cobalt, while the barren solution is evaporated to crystallize ammonium sulfate for sale as fertilizer.

At the end of a densification cycle when the powder has reached the desired particle size and density, the whole contents of the autoclave are discharged under pressure to a cone-bottomed flash tank. The solution is drawn off and the nickel powder is withdrawn from the bottom of the tank as a slurry containing 95% solids. The powder is washed with water and collected on a vacuum filter. The filter cake is dried in a rotary dryer fired with natural gas. The powder is either marketed as such or is converted to briquettes by mixing with an organic binder and pressing in briquetting rolls.

The "green" briquettes are sintered and desulfurized at 950 °C in a reducing atmosphere.

The powder typically analyzes 99.8% Ni, 0.08% Co, < 0.001% Cu, 0.002% Fe, 0.001% C, 0.025% S, and 0.02% O₂.

This process for recovering nickel powder from solution can be used in combination with the ammonia pressure leaching of nickel concentrates and mattes (as at Sherritt Gordon and Western Mining Corporation), with the acid pressure leaching of nickel-copper mattes (as at Impala Platinum and in the former Amax operation at Port Nickel), and with the Caron process for treating nickel laterites (as at Nonoc in the Philippines).

12.7 Beneficiation of Oxide Ores [1]

As described earlier, nickel oxide ores occur in two types: a limonitic type which occurs in the upper zone of a lateritic deposit, in which ferric oxide materials are predominant, and a silicate, or "garnierite" type, occurring at greater depth in the deposit, which has a lower iron content, but is usually richer in nickel than the limonite, and contains high levels of magnesium and silica. In nickeliferous limonite (Fe,Ni)O(OH)·*n*H₂O the nickel oxide is mainly present in solid solution with the iron oxides. In nickeliferous silicate, nickel, iron, and cobalt oxides occur in varying proportions, generally replacing part of the magnesium oxide in the serpentinite [Mg₆Si₄O₁₀(OH)₈].

Most deposits contain both types of ore. Usually it is possible to separate the ore by selective mining and screening into an iron-containing limonite fraction and a magnesium silicate fraction enriched in nickel. The metallurgy of nickel oxide ores differs from that of sulfides in that oxide ores are not amenable to most of the standard mineral beneficiation methods due to the chemical dissemination of the nickel in the oxide minerals. Screening may be used to reject the oversize, less weathered fragments that contain less nickel, but

this provides only a minor degree of upgrading.

In most cases the ore is treated directly by a pyrometallurgical or hydrometallurgical process. However, two processes have been developed in which the nickel is first converted by high-temperature treatment to a metallic phase, which can then be separated from the bulk of the ore by standard mineral beneficiation techniques. These processes are the Nippon Yakin Oheyama process (which was based on the Krupp-Renn process developed in Germany in the 1930s to produce iron from otherwise uneconomic low-grade iron ores) and the MINPRO-PAMCO segregation process.

12.7.1 Nippon Yakin Oheyama Process

Nippon Yakin Kogyo produces 12 000 t/a nickel as low-nickel ferronickel from silicate ores (2.3–2.6% Ni, 12–15% Fe), imported from New Caledonia, the Philippines, and Indonesia, at its Oheyama works in Japan [83]. The ore is ground and mixed with anthracite, coal, and flux, and briquetted. The briquettes are fed continuously through a rotary kiln, countercurrent to a flow of hot gas produced by the combustion of coal. As the temperature rises from 700 °C to 1300 °C, the charge is successively dried, dehydrated, and reduced. As the charge begins to melt, smelting occurs in the semifused state to form coalesced particles of spongy ferronickel (known as luppen, from the Krupp-Renn process) interspersed in a viscous slag phase. The kiln discharge is quenched in water and the luppen are separated from the slag by grinding, screening, jigging, and magnetic separation. Nickel recovery from ore is typically 95%.

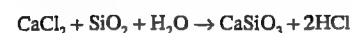
A major advantage of this process is that the ferronickel product is recovered in the form of 2–3 mm particles containing 22% Ni + Co, 0.45% S, 0.03% C, and 0.02% P which can be used directly in the AOD steel making process, without further upgrading or refining. Although the process is energy intensive, the major energy sources used are cheap anthra-

cite and coal, and no high cost electrical energy or oil is used for heating. Consequently, energy costs are relatively low.

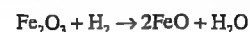
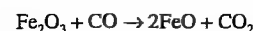
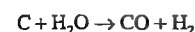
12.7.2 Segregation Processes

The segregation process [84, 85] was developed to recover copper from refractory minerals such as silicates, and has been applied with limited success on a commercial scale in Africa. Research has shown that the technique can be applied to the production of ferronickel from several types of nickel laterite ore, but the process has not yet been successfully applied on a commercial scale.

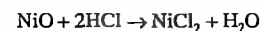
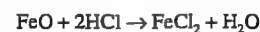
In the segregation process the ore is treated with a halide such as calcium chloride and a reductant such as coke at temperatures well below the melting range (950–1100 °C). Under these conditions the halide reacts with silicates and water vapor to form hydrogen chloride.



Iron(III) oxide is reduced to iron(II) oxide by hydrogen and carbon monoxide, which are formed in the reaction between coke and water.



The gaseous hydrogen chloride chloridizes both nickel oxide and iron(II) oxide to form the volatile metal chlorides.



The metal chlorides are reduced to metal by reaction with hydrogen at the surface of the coke particles,



releasing hydrogen chloride to react with further nickel and iron oxides. The ferronickel collects on the particles of coke and can be separated from the silicate phases by grinding and magnetic separation.

A major obstacle to the commercial development of this process has been the lack of a suitable reactor. The most promising ap-

proach, which was successfully tested at a rate of 1 t of ore per hour in 1981–1983, is the MINPRO-PAMCO segregation process. The reactor employed was a 850 kW former autogenous grinding mill, which was relined with two courses of refractory brick to permit operation at 950 °C.

In the pilot testwork, a nickel ore containing 2.3% Ni and 13.2% Fe was preheated in a rotary kiln to 950 °C, and treated in the segregation reactor with 40 kg calcium chloride and 20 kg coke per tonne of ore. The reactor discharge was cooled and ground prior to magnetic separation to yield a ferronickel product grading 59% Ni and 29% Fe, and a tailing with 0.45% Ni. Further upgrading to 68% Ni was shown to be possible with additional grinding and magnetic separation steps. Energy savings of 25–30% over the conventional smelting process have been projected by the developers of the process.

12.8 Pyrometallurgy of Oxide Ores

Nickel laterite ores have historically been treated almost exclusively by smelting processes, and except for Cuba, where nickel ore treatment is all essentially hydrometallurgical, the industry is still predominantly pyrometallurgical. The development of nickel oxide ore smelting has drawn heavily on iron and steel metallurgy for ferronickel production and on copper metallurgy for nickel matte production [1, 7, 8, 29].

The separation of nickel from the refractory oxides is relatively simple because there are large differences in the free energies of formation of nickel oxide and the gangue components such as silica and magnesia. Adjustment of the reduction conditions permits the complete reduction of nickel oxide while limiting the degree of reduction of iron oxide, but a total separation of nickel from iron by selective reduction is not possible. Two major process routes have been developed to overcome this problem.

In ferronickel production, the nickel oxide and part of the iron oxide are reduced to metal in an electric furnace. The fraction of iron reduced to metal is a function of the reduction potential of the system, so that ores with a low Ni/Fe ratio can be smelted to yield an acceptable ferronickel grade.

In nickel matte production, the ore is smelted with a reductant, a flux, and a source of sulfur, which may be gypsum, a sulfide mineral, or elemental sulfur. Most of the nickel and a large portion of the iron are reduced and sulfidized to form a low-sulfur matte phase. Iron removal can then be accomplished by fluxing and selective oxidation of the iron in a converter to produce a nickel matte containing over 75% Ni, 20–22% S, and less than 1% Fe.

The smelting of nickel silicate ores in blast furnaces was developed by Société Le Nickel

(SLN) in New Caledonia in the 1870s [86]. Initially, attempts were made to produce ferronickel, but after encountering difficulties in eliminating sulfur from the product, the operation switched to the production of nickel iron sulfide matte. The furnace matte was blown to give a low-iron converter matte, which was shipped to Europe or North America where it was dead roasted to remove sulfur and reduced in briquette form with charcoal to metal rondelles. The SLN introduced electric furnace smelting of nickel silicate ores to ferronickel in 1958, using a furnace design developed by Elkem–Spigerverket of Norway, and most present-day ferronickel smelters use processes based on this technology [87].

Several of the world's major nickel laterite smelters are listed in Table 12.12 together with details of their ore and product nickel grades and production capacities.

Table 12.12: Nickel laterite smelters.

Smelter	Ore grade, % Ni	Product		1988 production, t/a Ni
		Type	Grade, % Ni	
SLN, New Caledonia	2.70	Fe–Ni matte	25 78	37 000 10 000
P.T. Inco Indonesia	1.97	matte	79	28 000
Pacific Metals, Japan	2.40	Fe–Ni	14–22	25 000 ^a
Falconbridge, Dominican Republic	1.75	Fe–Ni	38	29 300
Cerro Matoso, Colombia	2.90	Fe–Ni	45	19 000
LARCO, Greece	1.25	Fe–Ni	24–30	13 000
Hyuga Smelter, Japan	2.40	Fe–Ni	20–25	12 000 ^a
Orsk, former Soviet Union	1.02	matte	77	16 000
Nippon Mining, Japan	2.40	Fe–Ni	20	10 000 ^a
Glogovac, Yugoslavia	1.32	Fe–Ni	24	5 500
P.T. Aneka Tambang, Indonesia	2.25	Fe–Ni	25	4 800

^a 1985 production data.

12.8.1 Ore Pretreatment

Nickel laterite ores have high moisture contents (typically up to 45%) as well as chemically bound water in the hydroxide form. All ore treatment plants use dryers, usually direct-fired rotary units operating at about 250 °C, which reduce the moisture content only to 15–20% to minimize dusting during drying and subsequent smelting. Calcining to dehydrate the ore and prereduction prior to electric fur-

nace smelting are generally carried out in countercurrently fired rotary kilns. Chemically bound water is released above ca. 400 °C, and reduction of the oxides to metal starts at 500–600 °C. The maximum temperature reached in the kiln is generally limited to 800–900 °C because of the tendency of the ore to agglomerate and form accretions on the furnace walls. Dehydration and prereduction of the ore in the kiln prior to smelting, optimizes the utilization of energy available from the re-

ductants and fuel, thus reducing energy consumption in the smelting operation.

12.8.2 Smelting to Nickel Matte

Low-iron nickel sulfide matte has long been produced from oxide nickel ores by reduction and sulfidation in a blast furnace. This process is still practiced in Russia at three smelters in the Urals, but the blast furnace has given way to the electric furnace smelting process in New Caledonia and in the P. T. Inco operation in Indonesia.

12.8.2.1 Blast Furnace Smelting

The blast furnace production of nickel matte was practiced by SLN at its Doniambo smelter in New Caledonia from 1880 until 1972. The nickel silicate ore was blended with calcium sulfate and coke and reduced directly to matte in the blast furnace. The low-grade furnace matte was then blown to 78% Ni and 20% S in a converter [88].

At the Yuzhuralnikel Combine at Orsk¹ in Russia, nickel silicate ores, averaging 1.02% Ni, 15.4% Fe, 10% MgO, and 49% SiO₂, are blended with ground coke, limestone, pyrite (0.1% Cu content), and recycled converter slag and sintered at 1100–1200 °C in one of five 75 m² downdraft sinter machines. The resulting sinter is crushed and smelted in one of eleven low (5 m height) shaft furnaces using 24% oxygen enriched air. The furnace matte, containing 17% Ni, 54% Fe, and 21% S is tapped at 1200 °C and blown in Peirce–Smith converters to a high-grade matte (77% Ni, 2.5% Cu, 0.2% Fe, 21% S).

The converter slag is cleaned to reduce its nickel and cobalt contents in a two-stage contact with molten furnace matte, and the cleaned slag is recycled to the shaft furnaces. The converter matte is cast, ground, and roasted in fluidized-bed roasters to eliminate sulfur and is then treated in a chloridizing roast in a rotary kiln, followed by acid leaching to remove copper. The leached nickel ox-

ide is reduction smelted with coke and the metal is granulated. The Orsk combine produces 16 000 t/a of nickel granules analyzing 98.5% Ni, 0.5% Co, 0.55% Cu, and 0.5% Fe from its exceptionally low-grade nickel laterite ore feed [49].

12.8.2.2 Matte Production from Ferronickel

SLN now produces nickel matte from crude ferronickel (24% Ni + Co, 69% Fe, 2% C, and 0.25% S) by means of a sulfidizing treatment with elemental sulfur in a Peirce Smith converter [89]. After sulfidizing, the matte is blown with air to oxidize iron, which is slagged off with silica flux in two stages, to produce a matte containing 75–80% Ni, 0.1 to 4% Fe, and 20% S. The cobalt content ranges from 0.4% in matte containing 0.1% Fe, to 1.2–1.7% Co in matte containing 4% Fe. This matte is shipped to the SLN nickel refinery at Le Havre-Sandouville in France, where it is refined to high-grade electrolytic nickel. Cobalt is recovered separately in the refilling process.

12.8.2.3 Inco Selective Reduction Smelting Process [90–94]

Inco's process for the production of nickel matte from laterite ores was developed for projects in Indonesia and Guatemala which started operation in 1977. The ore is dried and then calcined and partially reduced in a rotary kiln at 750–800 °C. Reduction is accomplished by adding coal to the kiln feed and by lancing high-sulfur oil into the ore bed. The hot calcine is smelted in an electric furnace. The bulk of the sulfur required to form a matte is added as molten elemental sulfur either to the kiln discharge, or directly to the electric furnace discharge. The resulting furnace matte is finally upgraded to the product matte in an air-blown converter.

12.9.1 Caron Process

The reduction roast and ammonium carbonate leach process was patented by M. H. CARON in 1924, but the first commercial application of the process was not initiated until World War II, when a plant was constructed at Nicaro, Cuba. The ore is first dried to about 5% moisture and is then selectively reduced in a multihearth roaster. The reduced calcine is cooled under nonoxidizing conditions and leached in ammoniacal ammonium carbonate solution to selectively extract nickel and cobalt. The pregnant leach liquor is then boiled to strip ammonia and carbon dioxide, causing the nickel and cobalt to precipitate as basic carbonates. The mixed nickel cobalt basic carbonate can be calcined to a nickel oxide product or can be refined to nickel powder or cathode. Details of a number of operations using the Caron process are given in Table 12.14.

Table 12.14: Commercial Caron process plants.

Operation	Design capacity, t/a Ni	Feed ore, %		Product type
		Ni	Co	
Nicaró, Cuba	22 500	1.40	0.10	NiO sinter
Queensland Nickel, Australia	18 000	1.35	0.11	NiO rondelles NiS-CoS
Nonoc, Philippines	30 000	1.22	0.10	Ni powder NiS-CoS
Punta Gorda, Cuba	30 000			NiO sinter
Tocantins, Brazil	5 000	1.60	0.14	Ni cathode
Elbasan, Albania	3 000			NiCO ₃

The original plant at Nicaro, built and operated by the Freeport Sulfur Company [1, 86], for the U.S. Government, was commissioned in 1944. It was closed down in 1947 as uneconomic under peacetime conditions, despite having achieved a production rate of 14 500 t of nickel as nickel oxide in 1946. However nickel recovery from the ore had never exceeded 70%. It was reopened in 1952 for the U.S. Government under the operating management of a joint venture of the National Lead Company and Fomento de Minerales Cubanos. Its production capacity was increased to 22 500 t/a Ni in 1957, and in 1960 it was nationalized by the Cuban Government.

Production is believed to have ranged from 16 000–20 000 t/a Ni during the 1970s and 1980s [95].

Freeport was also a member of the joint venture which constructed the Queensland Nickel refinery near Townsville, Australia in 1974, which drew heavily on the design and operating experience gained at Nicaro [96]. A second Caron plant in Cuba was built by the Cuban Government with Soviet assistance in the early 1980s at Punta Gorda, near Moa Bay. The first of three processing lines was commissioned in 1986 and by the end of 1988 production was reported to have reached 10 000 t/a Ni as nickel oxide. A third Cuban Caron plant is under construction in the same area at Las Camarioca, scheduled to start-up in 1995 [97].

The other large Caron plant was built by Marinduque Mining and Industrial Corporation on Nonoc Island in the Philippines with technical assistance from Sherritt Gordon [98, 99]. The Nicaro process was adapted by Sherritt to increase nickel and cobalt extractions and to produce hydrogen-reduced powder from the basic nickel carbonate.

The Nonoc nickel refinery was commissioned in 1974 and reached a production rate of around 22 000 t/a Ni in 1977, at a nickel recovery of 78% Ni. This plant was closed in 1986 after several years of declining operation due to adverse economic conditions. There are currently (1989) plans to refurbish the process plant and resume operation in the early 1990s. Both the Queensland Nickel and the Marinduque nickel operations were designed to recover cobalt separately as a by-product by precipitating a mixed cobalt-nickel sulfide prior to precipitation of basic nickel carbonate.

The Companhia Niquel Tocantins plant in Brazil began production of nickel cathode from basic nickel carbonate in 1981 and was scheduled to increase capacity to 10 000 t/a Ni by 1990 [100]. The small Caron plant at the Elbasan metallurgical complex in Albania ships its basic nickel carbonate product to the Severonikel Combine in the former Soviet Union for refining to metal.

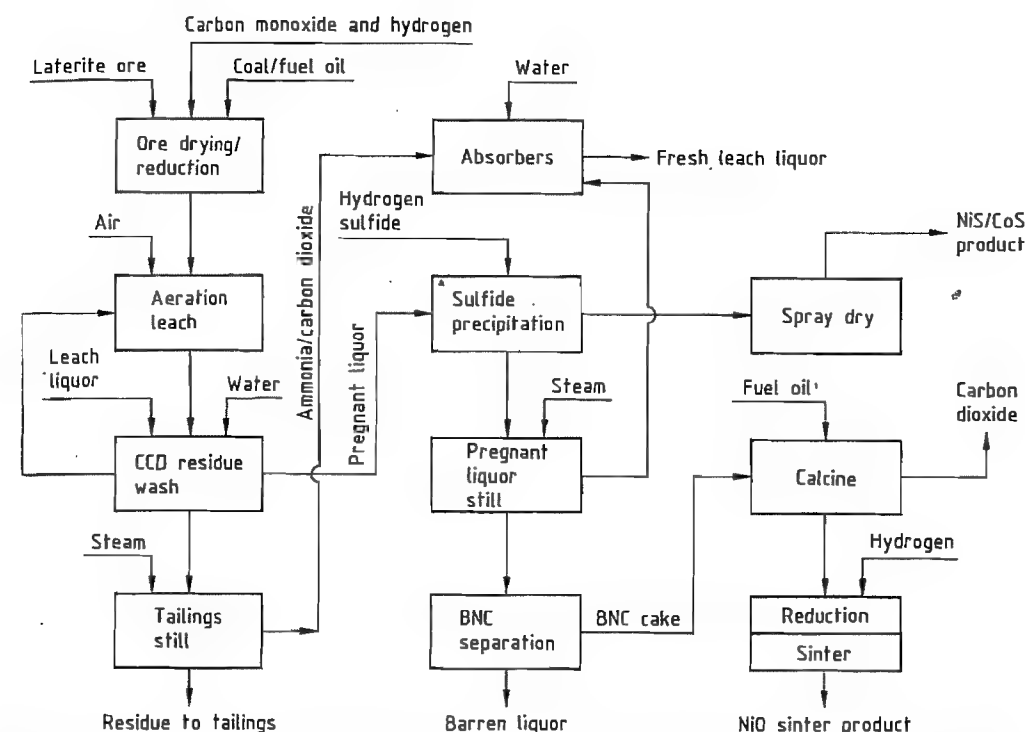
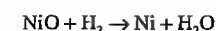


Figure 12.20: Flow sheet of the Queensland Nickel laterite refinery. CCD = Countercurrent decantation; BNC = Basic nickel carbonate.

Industrial practice is illustrated by the following description of the Queensland Nickel process, which closely resembles the original Nicaro process [1] except for the addition of a cobalt recovery step. The flow sheet of this plant, which was designed to treat 5700 t/d of ore from the Greenvale ore body is outlined in Figure 12.20 [96, 63].

The blended ore (1.35% Ni, 0.11% Co, 25% Fe, 10% MgO) is first dried in one of three rotary dryers to about 5% moisture content. The dried ore is then ground in a ball mill and blended with fuel oil as a reductant, before being fed to one of ten seventeen-hearth Herschhoff roasters, where it is roasted under reducing conditions at 700–760 °C with a retention time of ca. 90 min. The ore is heated by hot reducing gas (CO + H₂) formed by the combustion of fuel oil in a deficiency of air in the ten combustion chambers on each roaster. The reduction potential of the gas phase is regulated so that most of the nickel and cobalt in

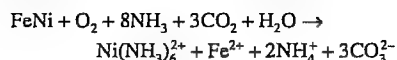
the ore are reduced to the metallic state (as a ferronickel alloy) and the iron(III) oxides are reduced to magnetite without significant reduction of the iron oxides to iron(II) oxide or to the metal.



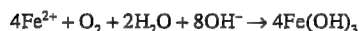
As a result the nickel and cobalt are rendered amenable to ammoniacal leaching while the iron remains as insoluble oxides or silicates. Typically 80–85% of the nickel content of the ore is converted to the metallic form. Any nickel oxide which is not reduced to metal is rendered insoluble under the roasting conditions by incorporation into the silicate minerals. Good control of the roasting conditions is therefore essential for optimal nickel recovery in the process.

The reduced ore is cooled in a nonoxidizing atmosphere, to avoid reoxidation of the nickel, and is quenched and leached in ammoniacal

ammonium carbonate solution containing 7% NH_3 and 4% CO_2 . Leaching is carried out in three trains of four mechanically agitated, air-sparged leaching tanks at a pulp density of ca. 20% solids. The leaching reactions can be represented by the following equation:



The iron(II) is further oxidized and precipitates as iron(III) hydroxide:



However, significant losses of cobalt occur by coprecipitation with the iron hydroxide.

The pregnant liquor is separated from the leached ore in a seven-stage countercurrent decantation thickener circuit using ammoniacal solution as the washing medium. The washing efficiency is typically 99%. Ammonia is recovered from the washed leach residues by steam stripping, and the barren solids are discarded. The pregnant liquor recovered from the wash circuit, which contains 10 g/L Ni and 0.5 g/L Co, was formerly treated with ammonium hydrogen sulfide in a pipeline reactor to precipitate virtually all of the cobalt and about 10% of the nickel. The mixed sulfide product (15% Co, 40% Ni) was thickened, washed, and spray dried, and sold for cobalt and nickel recovery elsewhere. Ammonia and carbon dioxide were then stripped from the cobalt-free solution by direct stream injection to precipitate basic nickel carbonate.

Since 1988, the pregnant liquor has been treated by solvent extraction to separate nickel and cobalt [101]. An organic reagent (LIX 87 QN) is used to extract nickel selectively from the pregnant liquor. The nickel is recovered from the solvent by stripping with a more concentrated ammoniacal ammonium carbonate solution. Basic nickel carbonate can then be precipitated from the strip liquor by steam injection to remove ammonia and carbon dioxide. Copper sulfide is precipitated from the raffinate and refined elsewhere.

The basic nickel carbonate is recovered by thickening and filtration, and the wet filter cake, containing about 50% moisture, is dried

and calcined at 1300 °C in an oil-fired rotary kiln to yield nickel oxide. The nickel oxide calcine (77% Ni) is upgraded by partial hydrogen reduction to yield nickel oxides containing 85, 88, or 90% Ni, which are compacted to rondelles and sintered for market.

By the late 1980s the Greenvale nickel ore body, which had provided the sole feed to the Queensland Nickel refinery since 1974 was rapidly becoming depleted, and the operation started to treat laterite ores imported from New Caledonia and Indonesia.

The major difference between the process flow sheets used by Queensland Nickel and Marinduque/Nonoc was the production of refined nickel powder in the latter [99]. Basic nickel carbonate was redissolved in ammoniacal ammonium sulfate solution and metallic nickel powder was precipitated by reduction with hydrogen under pressure at 200 °C. The nickel powder typically analyzed 99.8% Ni, 0.08% Co, 0.01% Fe, 0.007% Cu, 0.006% C, and 0.004% S. By comparison the nickel oxide sinter produced prior to 1960 in the Nicaro plant, which had no cobalt separation step, analyzed 88% Ni, 0.7% Co, 0.04% Cu, 0.3% Fe, 0.05% C, 0.05% S, and 7.5% O_2 . In the Tocantins refinery a crude basic nickel-cobalt carbonate is redissolved in spent sulfuric acid electrolyte, and after purification by sulfide precipitation to remove cobalt and copper, the solution is treated by electrowinning to yield nickel cathode [63].

The Caron process is very energy intensive, and this factor proved a major economic handicap for the Queensland Nickel and Marinduque/Nonoc plants, which were both designed prior to 1973, with their heavy reliance on fuel oil for ore drying, reduction, and power generation. The fossil fuel energy requirements for the process for ore drying and reduction, and power and steam generation amount to ca. 6.7 GJ/t of dry ore, with an additional 200–250 MJ/t of electrical power. The Queensland Nickel plant originally consumed 900 t/d of fuel oil to treat 5700 t of ore. The distribution of oil consumption is as follows [102]:

Ore drying	14%
Steam and power generation	35%

Ore reduction roasting	47%
Nickel carbonate calcining	4%

Both Queensland Nickel and Marinduque/Nonoc converted their ore drying and steam and power generation facilities to use coal in place of oil in the early 1980s, with substantial economic benefit. However, conversion of the roasters to coal firing was not considered to be technically feasible. The Tocantins plant in Brazil makes extensive use of local eucalyptus wood as fuel in its ore treatment plant.

12.9.2 Pressure Leaching with Sulfuric Acid [1]

Because of the naturally high moisture content of limonite minerals (20–50% H_2O), it would be advantageous if the ore drying and reduction roasting steps, which together account for over 50% of the energy consumed in the Caron process, could be avoided, and the ore leached directly. However direct attack by the common mineral acids under ambient conditions is unselective and total dissolution of the ore results, with uneconomically high acid consumption. Fortunately, leaching of the ores in sulfuric acid at high temperature (> 250 °C) and pressure is highly selective since nickel and cobalt are stable as soluble sulfates, while iron(III) sulfate hydrolyzes and precipitates as a hydrated iron(III) oxide. Offsetting the energy savings in this type of process are the increased costs of construction materials capable of withstanding the highly corrosive environment of the high-temperature acid leach.

The applicability of the acid leach process is limited to those ores which do not contain substantial levels of other acid consuming minerals such as magnesia. It was for this reason that Freeport did not select an acid leaching process when seeking a process to treat the Nicaro ores (8% MgO). However when the same company subsequently developed the low-magnesia (1.7% MgO) limonitic ore body at Moa, Cuba, the sulfuric acid leach process was selected since it offered much higher (90% or more) recoveries for both

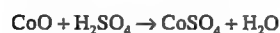
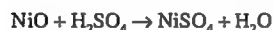
nickel and cobalt, with relatively low acid consumption. Although this process has been applied on a commercial scale only in the one plant at Moa, considerable process development effort was devoted during the 1970s to improving the economics and extending the applicability of the process to higher magnesia content ores, principally by Amax.

12.9.2.1 Moa Process

The plant at Moa was designed and built by Freeport in 1959 to produce 22 700 t/a Ni and 2000 t/a Co in the form of a mixed sulfide concentrate. The concentrate was to be refined to the pure metals in a separate plant which Freeport built at Port Nickel, Louisiana, where a cheap supply of natural gas was available. The Moa operation was nationalized in 1960 by the Cuban Government before construction was complete. It was recommissioned in mid-1961 with Soviet assistance, and since then the nickel-cobalt sulfide concentrate has been shipped to the former Soviet Union for further processing. The current production rate (1988) is believed to be 18 000 t/a Ni and 1600 t/a Co.

Although the original plant design is well documented, information on subsequent modifications is fragmentary. The following description is therefore based largely on accounts dating from 1960 [1, 95, 103–105]. The process flow sheet is shown in Figure 12.21. The ore, which consists mainly of goethite ($\alpha\text{-FeO}\cdot\text{OH}$), is slurried in water and screened to remove low-grade, oversize material, which is discarded. The fines fraction (< 1 mm) that forms the feed to the acid pressure leach averages 1.35% Ni, 0.15% Co, 48% Fe, 1.7% MgO, 9% Al_2O_3 , 3% Cr_2O_3 , and 4% SiO_2 in composition. It is leached at 45% solids pulp density with 98% sulfuric acid (240 kg H_2SO_4 /t dry ore) at about 245 °C and 4.3 MPa, with a retention time of 1–2 h. The acid is made on-site from elemental sulfur, and the waste heat from the acid plant is used in the leaching circuit. Leaching is carried out in four leaching trains each containing four large vertical autoclaves, which are lead- and brick-lined with titanium internal fittings. Agitation

is achieved by injecting high-pressure steam into a draft tube at the bottom of the vessel. Heat is recovered from the autoclave discharge slurry for use in preheating the cold feed slurry. Under these conditions, about 94% of the nickel and cobalt dissolve, while iron solubility is limited to about 1 g/L.



The leach liquor typically contains 6 g/L Ni, 0.5 g/L Co, 2 g/L Mn, 0.8 g/L Fe, 0.4 g/L Cr, 2.5 g/L Mg, 2 g/L SiO_2 , 3 g/L Al, and 30 g/L H_2SO_4 . The liquor is separated from the leach residue (0.08% Ni, 0.01% Co, and 51% Fe) by countercurrent decantation (CCD) washing with water in a six-stage thickener circuit. The washed residue is stockpiled for possible future use as iron ore.

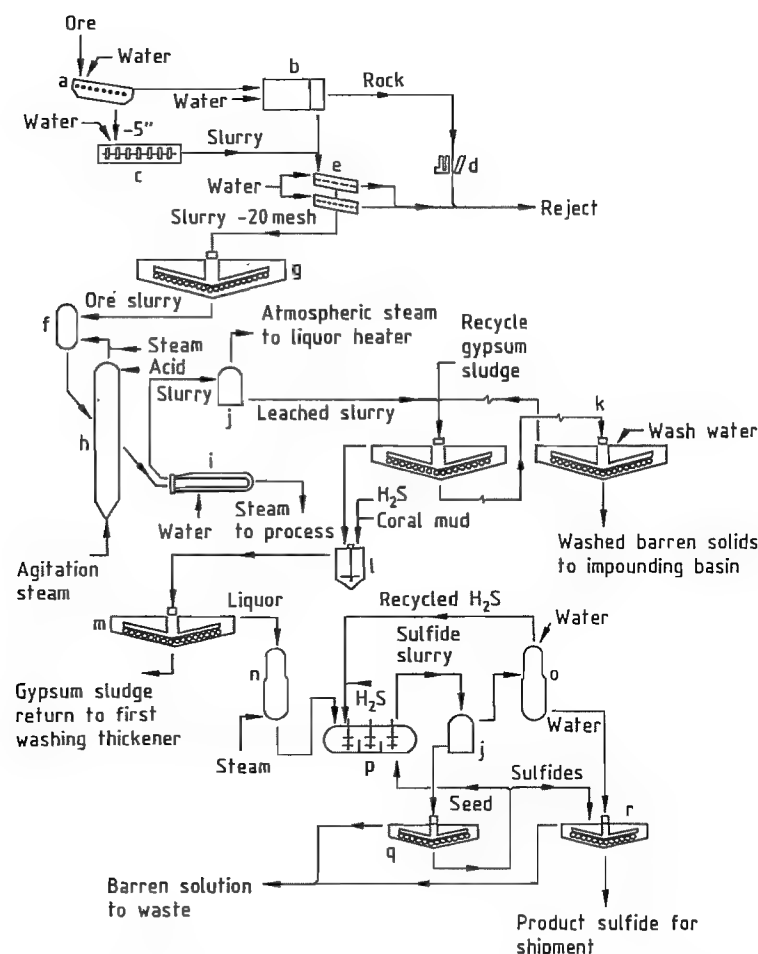
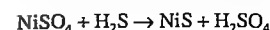


Figure 12.21: Flow sheet of the Moa nickel laterite plant: a) Shaking grizzly; b) Cylindrical scrubber; c) Log washer; d) Jaw crusher; e) Screens; f) Slurry heaters; g) Storage thickener; h) Leaching autoclaves (4 in series); i) Slurry cooler; j) Flash tank; k) Washing thickeners (6-stage CCD); l) Neutralizing tanks (4-stage cascade); m) Gypsum thickener; n) Heaters; o) Gas cooler; p) Precipitation autoclave; q) Sulfide thickener; r) Washing thickeners (2-stage CCD).

The pregnant solution is treated with coral mud (calcium carbonate) to neutralize the acid and precipitate most of the dissolved iron, aluminum, and manganese by hydrolysis. The precipitated sludge is recycled to the wash circuit and joins the leach residue for disposal. The neutralized solution typically contains (g/L): 3.5–4.0 Ni, 0.3–0.4 Co, 1.0 Mn, 0.3 Fe, 0.4 Cr, 2.5 Mg, 1.0 SiO_2 , and 3.0 Al at pH 2.5. Nickel and cobalt are recovered from solution in 98–99% yield by precipitation at 120 °C with hydrogen sulfide at a pressure of 1.1 MPa in a three-compartment, brick-lined autoclave.



The barren solution typically contains (g/L): 0.05 Ni, 0.01 Co, 1.0 Mn, and 7 H_2SO_4 . The nickel cobalt concentrate contains 55% Ni, 5% Co, 0.7% Fe, 0.2% Cu, 1.0% Zn, and 35% S.

The refinery built by Freeport in Louisiana to treat the concentrate employed pressure hydrometallurgy and hydrogen reduction to separate and refine nickel and cobalt. This plant was being commissioned when the Cuban nickel industry was nationalized in 1960, and was never used for the purpose for which it was designed. Currently (1989) the total nickel-cobalt concentrate production from Moa Bay is shipped to the former Soviet Union, where it is treated at a smelter in the Urals to produce nickel-cobalt anodes analyzing 87% Ni, 8% Co, 2% Fe, and 0.7% Cu. The anodes are electrorefined at the Yuzhuralnikel Combine at Orsk in a conventional sulfate chloride electrolyte system. The nickel is recovered as high-grade electrolytic nickel, and cobalt is separated from anolyte by chlorine precipitation for subsequent processing to metal [49].

Energy consumption in the Moa acid leach process is relatively low because over half the steam requirement for the leach is provided by waste heat recovered from the sulfuric acid plant. The fuel oil requirement for the generation of power and steam has been estimated at about 40 kg/t of dry ore, which is only 20% of the fuel requirement for the Caron process. However, this energy benefit is frequently out-

weighed by the high consumption of sulfuric acid which depends directly on the magnesia content of the ore [106].

12.9.2.2 Amax Acid Leach Process

The Amax acid leach process for the treatment of laterite ores [107–109] was developed, on the basis of the Moa process, with the object of increasing metal recoveries while decreasing acid and energy consumption. The process was tested extensively in pilot plant and prototype plant campaigns between 1975 and 1981, for a potential new project in New Caledonia which was subsequently abandoned.

In the Amax process (Figure 12.22) the ore is divided by selective mining or screening into a low-magnesia limonitic fraction and a smaller fraction of high-magnesia serpentinic ore. The finer limonitic fraction is leached directly in the pressure leach at 270 °C, while the high-magnesia fraction is first calcined and then preleached at atmospheric pressure with the leach liquor from the countercurrent decantation wash circuit, before it goes to the pressure leach. Essentially stoichiometric utilization of the acid is achieved by this countercurrent leaching of the high-magnesia ore. The overall acid requirement is thus reduced substantially, and the need for a separate alkaline neutralizing agent (e.g., coral mud at Moa) is eliminated. Metal extractions of 94–97% are normally achieved with a 20-min retention time in the pressure leach at 270 °C.

A major saving (up to 70%) in energy consumption in the leaching step is achieved by using indirect heating of the feed slurry with flash steam recovered from the autoclave discharge slurry. By using this technique in place of direct steam sparging, the concentration of metals in solution is substantially increased, and the size and cost of subsequent processing steps is reduced. Overall the requirement for fossil fuel is estimated to be only 50% of that for the Moa operation. A further simplification of the process was achieved by improving mass transfer in the sulfide precipitation step so that it could be operated at a lower pressure

of 0.2 MPa compared with 1.1 MPa at Moa Bay. The Amax acid leach process is claimed to be economically viable over a wide range of laterite ore compositions, with magnesia contents as high as 15% MgO.

12.10 By-Product Cobalt

All nickel ores, whether sulfide or oxide, contain significant amounts of cobalt that can potentially be recovered as a valuable by-product. Overall, however, the recovery of cobalt from nickel ores is very low, and the nickel industry provides less than 30% of world cobalt production. The greater part of world cobalt production arises from the copper operations in Zaire and Zambia.

No cobalt recovery at all is possible in ferronickel smelting, where the cobalt is distributed between the discard slags and the ferronickel product, in which it merely represents an impurity. The same comments apply to class II nickel products such as nickel oxide sinter, made by the smelting of sulfide concentrates or by the Caron process without a cobalt separation circuit.

Cobalt is normally recovered in high yield as a by-product of carbonyl, electrolytic, or hydrometallurgical refining of nickel metal or matte. However, even in these cases the over-

all recovery of cobalt from the ore is low, since most of the cobalt is lost to the slag phase in the prior smelting processes. Cobalt recovery in the converting operation depends critically on the final iron content of the matte. Typically if the matte is blown to less than 1% Fe, over 75% of the cobalt reports to the slag phase and is effectively lost. If the conversion process is stopped at 3–5% Fe, however, over 75% of the cobalt remains in the matte, and can be recovered during subsequent refining.

In practice few nickel smelters are operated to maximize the recovery of cobalt. The SLN in New Caledonia and the Soviet smelters producing matte from laterites are notable exceptions. Slags are cleaned by contact with a high-iron matte, which becomes enriched in cobalt. The cobalt is then recovered by hydrometallurgical treatment of the enriched material.

Even in the ammonia pressure leaching of nickel sulfide concentrates, where the smelting step is bypassed, cobalt recovery is much lower than that of nickel, due to a strong affinity of the iron oxide residue for soluble cobalt. Probably the highest overall recovery of cobalt from nickel ores is achieved in the sulfuric acid pressure leaching of laterite ores, in which a cobalt recovery of 90% is possible.

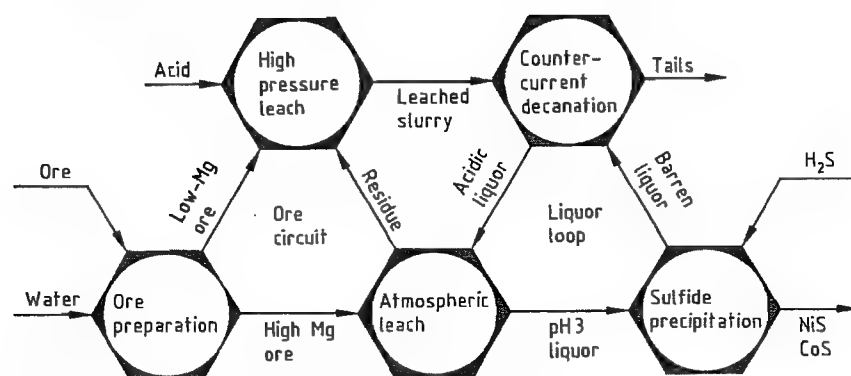


Figure 12.22: Flow sheet of the Amax nickel laterite process.

Table 12.15: Commercial forms of nickel [114].

Type	Composition, %						
	Ni	Co	Cu	Fe	C	S	O
Class I:							
Cathodes	> 99.90		0.005	0.002	0.01	0.001	
Pellets	> 99.97	5 ¥ 10–5	0.001	0.0015	< 0.10	0.0003	
Powder	99.74			< 0.10	< 0.10	< 0.010	< 0.15
Briquettes	99.90	0.03	0.001	0.01	0.01	0.0035	
Rondelles	99.25	0.37	0.046	0.022	0.022	0.004	0.042
Class II:							
Ferronickel	20–50	1–2		rest	1.5–1.8	< 0.3	#
Nickel oxide	76.0	1.0	0.75	0.30		0.006	rest

12.11 Recovery from Secondary Sources

Nickel-containing scrap from forming processes in fabricating plants and machine shops is an important source of feed material for the production of nickel-containing stainless steel. Typically, in the United States about 40% of the nickel used for stainless steel production is provided in the form of stainless steel scrap from outside sources. Recycled in-house scrap is not included in this estimate [110, 111]. Nickel-containing scrap falls mainly into the categories of stainless steels, superalloys, copper nickel alloys, and nickel itself. Usually scrap is recycled to a plant which produces the same type of alloy.

Inco established The International Metals Reclamation Company (INMETCO) at Ellwood City, Pennsylvania in 1978, to collect and convert nickel-containing waste materials from specialty steel companies into a stainless steel remelt material. This 40 000 t/a capacity plant treats various grades of scrap materials including flue dusts, scale and turnings, as well as stainless steel scrap, to produce 23 kg remelt pigs containing ca. 18% Ni and 8% Cr [112]. Falconbridge also started to recycle nickel- and cobalt-containing alloys to its primary nickel smelter in 1985 [113].

12.12 Market Products

Unlike copper, nickel is rarely used without further processing and so the mechanical or physical properties of nickel products are of

no significance, and nickel is marketed solely on the basis of its chemical composition. Nickel is marketed according to its chemical purity as either a Class I or a Class II product. Class I includes the high-purity products, electrolytic cathode, carbonyl refined granules and powder, and hydrogen-reduced nickel in powder or briquette form. Commercial nickel of this class is normally 99.7% pure or better [114].

Class II includes the various grades of ferronickel, nickel oxide, and metallized nickel oxide. Typical compositions for Class I and II products are given in Table 12.15. Class II nickel products, which normally sell at a discount to Class I nickel, became more popular during the 1970s, since the new stainless steel making techniques such as the AOD process can tolerate higher impurity levels in the feed materials. However this trend was reversed during the 1980s, during the period of oversupply and low metal prices, particularly for alloy steel production where Class I nickel was preferred [111].

Some nickel products are designed for specific applications, such as the 0.02% S content “S Nickel Rounds” produced by Inco as “active” anode material for the plating industry, and the special powders used in Ni–Cd batteries. Traditionally, electrolytic nickel cathodes are cut into 2.5 cm squares for market. Both the major producers of electrolytic nickel, Inco and Falconbridge, now produce electrolytic nickel in the form of “rounds” (Inco) or “crowns” (Falconbridge), by plating nickel onto specially masked cathode blanks, to pro-

duce discrete round deposits. These deposits can be stripped from the blanks and drummed directly without shearing, and are easier for the consumer to handle than sheared cathode.

12.13 Uses [111, 115–117]

The major first uses of nickel are summarized in Table 12.16. Stainless steel production accounts for over 50% of nickel consumption, followed by ferrous alloys, and nickel-base alloys. Electroplating takes only 11% of nickel consumption [118].

Table 12.16: Western-world nickel consumption: distribution by first use in 1987 [118].

First use	Distribution, %
Stainless steel	51
Alloy steels	12
Nickel-base alloys	15
Copper-base alloys	3
Plating	11
Foundry	5
Other	3

Table 12.17: Western-world nickel consumption: distribution by end use in 1987 [118].

End use	Distribution, %
Consumer products	25
Construction and machinery	13
Automotive industry	11
Chemical industry	9
Building and construction	6
Process industry	6
Electronics	6
Power industry	5
Petroleum industry	5
Aerospace	3
Nickel chemicals	2
Marine applications	2
Coinage	2
Other	5

A more detailed breakdown of nickel consumption by end use is given in Table 12.17. The consumer product category, which includes the stainless steel used in kitchen sinks, laundry equipment, furniture and tableware, as well as nickel-plated parts for bicycles, motorcycles, jewelry, eyeglass frames, and musical instruments, accounts for one quarter of

nickel consumption. The high strength of nickel stainless steels combined with light weight and low maintenance have contributed to their growing use in railway cars and road tank trailers in the construction and machinery category [117].

Nickel consumption dropped significantly during the 1970s in the automotive industry with the amount of nickel used in the average U.S. car falling from about 2 kg in 1970 to only 0.5 kg by 1985 [111]. The chemical industry is the fourth largest market for nickel, mainly in stainless steels for a multitude of applications.

Building and construction, the process industries, and the electronics industries each accounted for about 6% of nickel consumption in 1987. Stainless steel usage in architectural applications is increasing, as it is in environmental control equipment and food processing equipment. The growth rate of nickel usage in the electronics industry is greater than 10% per annum. Alloy 42, a nickel-iron alloy, is widely used in lead frames, while a copper-nickel-tin alloy C72500, is used in springs, clips, and terminals.

In the power industry, nickel-containing stainless steels are widely used in nuclear power stations and are increasingly being applied in scrubber systems for the removal of sulfur dioxide from the flue gases of oil- and coal-fired power stations. Nickel-containing materials are used in the petroleum industry in applications ranging from drilling bits to piping and process vessels in petrochemical plants, and to the construction of off-shore production platforms. In the marine category, nickel-containing materials are used in ships and in desalination plants. In the aerospace industry nickel is a key element in superalloys that resist stress and corrosion at temperatures of 1000 °C and above. These materials are used in gas turbine engines.

Nickel chemicals are used in the production of nickel catalysts for use in the hydrogenation of vegetable oils, in heavy oil refining, as nickel salts in electroplating, and for color enhancement in ceramics. Coinage alloys con-

taining nickel have been used since ancient times [3]. Today the 75 Cu–25 Ni cupronickel alloy is the most widely used, although Canada, the Netherlands, and the Republic of South Africa use pure nickel coinage, which is particularly durable.

In 1984, after several years of decreasing world demand for nickel, sixteen of the major nickel producers cooperated to set up the Nickel Development Institute (NiDI) with headquarters in Toronto, Canada. The NiDI has a mandate to increase the use of nickel. In this function NiDI has taken over the market development role which was performed very effectively by Inco from the 1920s until the mid 1970s, when a much reduced share of world nickel production and the depressed nickel market forced Inco to cut its activity in this area. The NiDI, which is international in scope, has set up technical information offices in North America, Europe, Japan, India, and Central and South America, backed by a worldwide network of consultants. The organization publishes a periodical applications oriented magazine, "Nickel", which has wide circulation, as well as sponsoring technical papers and a series of reference books on selected topics. The NiDI has initiated a wide range of market development and research programs to promote the use of nickel, and provides expertise and advice to users of nickel and nickel-containing products [115, 117].

12.14 Economic Aspects

[115, 118]

Western-world nickel consumption increased by an average of 6.5% per annum from 1945 to 1974, when it reached a level of 576 000 t (Figure 12.23). Consumption dropped sharply in 1975, and the demand for nickel remained flat for the next ten years, with annual rates fluctuating in the range 450 000–600 000 t/a. Although demand approached the 600 000 t/a consumption level in 1979 it was not exceeded until 1987 [119]. Western-world nickel consumption in 1987

and 1988 was 625 000 t and 640 000 t, respectively.

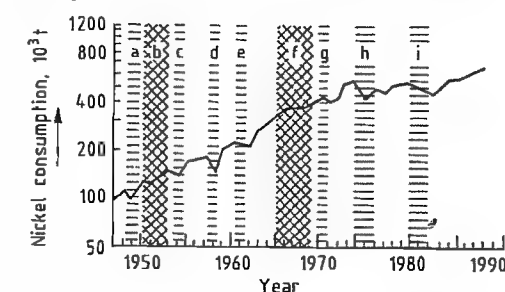


Figure 12.23: Western-world nickel consumption: a) 1949 recession; b) Korean war; c) 1954 recession; d) 1958 recession; e) 1961 recession; f) Vietnam war; g) 1971 recession; h) 1974–1976 recession; i) 1980–1982 recession.

The slowdown in the growth of nickel consumption in the mid 1970s coincided with a major increase in production capacity, when several laterite projects, which had been under development for five to ten years, came on stream. Many of these projects were heavily dependent on fuel oil and in consequence suffered a severe penalty when oil prices increased dramatically in 1973. During this period, nickel production by the Eastern-bloc countries also regularly exceeded consumption by 15 000 to 40 000 t/a, and substantial exports were made to Western markets.

By 1980 there were over forty nickel producers in 26 different countries, and the nickel price collapsed as the demand for nickel dropped in 1981 and 1982, and the producers fought for the shrinking market. Even the most cost efficient suffered heavy losses, and several higher cost producers were eventually forced to close permanently. The surviving operations sought to cut operating costs in every facet of nickel production, and as a result the nickel industry was much leaner and more cost efficient by the end of the 1980s.

When Western-world stainless steel production increased by 15% in 1987, the demand for nickel increased by over 10% from the relatively constant levels of 1984 to 1986. After more than ten years of depressed metal prices and production rates, the industry was unable to respond by increasing production

levels since producer inventories of metal had been run down to a minimum and most marginal capacity had been eliminated in the drive to reduce operating costs. The result was a two year period of inflated nickel prices, with the London Metal Exchange (LME) refined nickel cash price, which had averaged US \$1.60/lb in January 1987, peaking at \$10.84 in March 1988. The average price for the whole of 1988 was \$6.25/lb, and high prices continued through most of 1989 with an average price for the year of \$6.05. This development restored the financial health of the industry after many years of marginal or uneconomic operation.

The high nickel prices of 1988/89 raised concerns among both stainless steel and nickel producers that substitution of nickel-bearing materials by cheaper materials would be encouraged. Average industry operating costs in 1989 were estimated to be around US \$2/lb, while estimates of the capital expenditure required for a new integrated nickel project range upwards from US \$10/lb of annual capacity. A long-term nickel price of US \$4–5/lb, which would be needed to justify investment in new production capacity can be expected to depress demand and render new capacity unnecessary. Future increases in production thus appear more likely to come from the expansion of existing operations than from totally new projects.

Details of world nickel mine and smelter production by country for 1985 are given in Table 12.18 and the corresponding consumption breakdown is shown in Table 12.19. Table 12.20 provides a listing of the world's major nickel-producing operations.

For many years nickel was sold on the basis of posted producer prices, set to a large extent by Inco as the major producer. In 1979 the LME started trading in Class I nickel, and even though the LME handles only a relatively small percentage of total nickel production, it has since become the major factor in determining nickel price levels. Prices are quoted in US \$ per metric tonne of Class I metal.

Table 12.18: Production of nickel in 1993 [120].

Country	Production, 10 ³ t	
	Mine	Smelter/refinery ^a
Australia	64.7	50.4
Austria		3.5
Botswana	19.7	
Brazil	22.7	15.2
Canada	188.4	123.1
China	32.4	31.0
Colombia	20.2	20.2
Cuba	30.2	16.5
Dominican Republic	23.9	23.9
Finland	8.3	14.8
France		9.0
Greece	12.6	10.9
Indonesia	65.8	5.3
Japan		102.9
Korea		11.3
New Caledonia	98.1	36.9
Norway	3.6	56.8
Philippines	7.7	
Russia	180.0	190.0
South Africa	28.9	29.9
Taiwan		9.0
United Kingdom		28.0
United States	2.5	4.9
Yugoslavia	1.5	3.0
Zimbabwe	12.8	18.2
Total	824.0	814.7

^aIncluding ferronickel and nickel oxides as well as refined nickel.

Table 12.19: Consumption of nickel in 1989 [120].

Country	Consumption, 10 ³ t
Brazil	12.2
Canada	16.9
United States	132.2
<i>Other America</i>	5.0
China	45.0
India	13.0
Japan	156.7
Korea	33.2
Taiwan	21.0
<i>Other Asia</i>	8.1
Australasia	1.7
South Africa	11.0
Belgium	22.0
Germany	75.0
Finland	26.8
France	36.5
Italy	38.5
Russia	64.0
Spain	18.0
Sweden	22.8
United Kingdom	29.8
<i>Other Europe</i>	11.5
Total	825.0

12.15 Toxicology

The toxicology of nickel and its compounds and legislation pertaining to nickel and its compounds in the environment and workplace are discussed in detail in Section 12.17.5.

12.16 Alloys

Nickel forms mixed crystals over a wide range with copper, manganese, iron, chromium, and other metals. It is mainly used as an alloying element in many nonferrous materials and steels (approximately 2000) to improve their strength, toughness, corrosion resistance, and high-temperature properties. About 60 % of the primary nickel produced in the Western World is used in the production of stainless steels, and a further 13 % is used in the production of nickel-base alloys, including pure nickel semifinished products.

In 1988 primary nickel consumption by first use in the Western World broke down as follows (in %) [121]:

Alloy steels	6
Stainless steels	60
Nonferrous nickel-base alloys	13
Plating applications	10
Foundry industry	6
Other applications	5

12.17 Compounds

Of the worldwide production of nickel, only about 3 % is in the form of compounds if ferronickel, nickel oxide, and partially reduced nickel oxides used in the metallurgical industry are excluded.

The main uses of nickel compounds fall into four areas:

- **Electroplating.** This includes electroforming and electroless nickel plating as well as conventional nickel electroplating.
- **Catalysis.** Nickel, its alloys and compounds serve as catalysts for numerous chemical reactions. The main uses of nickel catalysts, prepared from nickel compounds, are in steam reforming, hydrocracking, and in hy-

drogenation reactions, including methanation.

- **Batteries.** There are various routes to the nickel hydroxide used as the active mass in nickel-cadmium batteries.
- **Pigments.** These include colorants in enamels, glassware, ceramics, and plastics.

Like all transition metals, nickel forms numerous complexes. These are of academic rather than industrial importance. Most nickel compounds are green; some are blue. Much information is available from the standard reference works [122–124] and a review [125]. There is an extensive review of the coordination chemistry of nickel in [126].

Nickel(II) amidosulfate, nickel sulfamate, $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$, is a highly soluble salt which is used in solution in the electrolyte for nickel electroforming processes, giving low stress deposits.

Commercially, it is available not as a solid but as a solution containing about 11 % nickel. This is usually prepared by dissolving nickel powder in a hot solution of sulfamic acid ($\text{HSO}_3 \cdot \text{NH}_2$), but soluble nickel oxide, nickel hydroxide, or nickel carbonate can also be used. Short reaction times are necessary because of the hydrolysis of sulfamic acid to sulfuric acid.

Nickel(II) ammonium sulfate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, can be crystallized as blue-green crystals from a solution containing the two components in the appropriate ratio. It has low solubility in water, ca. 25 g/L at 20 °C. The salt was formerly used in electroplating, but now its uses are very limited.

Nickel(II) Carbonate. Although a hydrated carbonate $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ and the anhydrous form NiCO_3 exist, the industrially important compound is the bright green, rhombic basic nickel carbonate approximating to $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. It is virtually insoluble in water, but dissolves in acids with evolution of carbon dioxide. Heating to above ca. 450 °C in air gives a reactive nickel oxide with a high specific surface area.

Table 12.20: Major nickel producers (1990).

Country	Company or location	Operations ^a	Estimated capacity, t/a
Australia	Western Mining	M,S,R	80 000
	Queensland Nickel	M,R	27 000
Botswana	BCL Limited	M,S	22 000
Brazil	Cia. Niquel Tocantins	M,R	10 000
	Codemin SA	M,S	6 500
Canada	Inco Limited	M,S,R	163 900
	Falconbridge	M,S	45 000
	Sherritt Gordon	R	25 000
China	Jianchuan	M,S,R	25 000
Colombia	Cerro Matoso SA	M,S	20 000
Cuba	Cubaniquel	M,R	52 000
Dominican Republic	Falcondo	M,S	32 000
Finland	Outokumpu Oy	S,R	18 000
France	Société Le Nickel (SLN)	R	13 000
Greece	LARCO SA	M,S	25 000
Indonesia	PT Inco Indonesia	M,S	45 400
	PT Aneka Tambang	M,S	10 000
Japan	Pacific Metals	S	40 800
	Nippon Yakin Kogyo	S, R	12 700
	Sumitomo Metal Min.	S, R	46 000
	Tokyo Nickel Co.	R	36 000
Korea	Korea Nickel	R	12 000
New Caledonia	Société Le Nickel (SLN)	M,S	50 000
Norway	Falconbridge Nikkelverk	R	67 000
Russia	Norilsk	M, S, R	300 000
	Ural Nickel	M, S, R	70 000
South Africa	Rustenburg Platinum	M,S,R	19 000
	Impala Platinum	M,S,R	12 000
	Western Platinum	M, S, R	2 000
	Pobugskoye	M, S	6 600
Ukraine	Inco Europe, Clydach	R	36 000
United Kingdom	Glenbrook Nickel	M, S	26 000
Yugoslavia	Kavardarci	M,S	28 000
Zimbabwe	Bindura Nickel	M,S,R	15 000
	Rio Tinto, Empress	R	6 500

^aM = mine; S = smelter; R = refinery.

Commercial basic nickel carbonate is made by precipitation from a nickel solution, usually the sulfate, with sodium carbonate. The exact composition depends on the temperature and the concentrations of the components in solution.

Basic nickel carbonate is used for pH adjustment in nickel electroplating baths, in catalyst production, and in the manufacture of some nickel pigments and specialty nickel compounds.

Demand for basic nickel carbonate has recently increased due to the use of zinc-nickel

plating of steel by the automotive industry. In one electroplating method, the nickel in solution is replenished by basic nickel carbonate.

It is also possible to prepare nickel carbonate by dissolving nickel in ammonium carbonate solution in the presence of air and carbon dioxide. Boiling off the ammonia and carbon dioxide precipitates basic nickel carbonate. This method forms part of the Caron process for the refining of nickel. The carbonate is further processed to nickel oxide or nickel metal.

Nickel(II) Halides. Nickel forms dihalides with all four halogens, and each dihalide forms one or more hydrates. Only the chlorides are of industrial importance, particularly the hexahydrate $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, which is available either as a solid or as a concentrated solution.

Table 12.21 lists some properties of the dihalides and the hydrate usually encountered. Known hydrates are $\text{NiF}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot x\text{H}_2\text{O}$, ($x = 2, 4, 6, 7$). $\text{NiBr}_2 \cdot x\text{H}_2\text{O}$ ($x = 2, 3, 6, 9$), $\text{NiI}_2 \cdot x\text{H}_2\text{O}$ ($x = 4, 6$). Nickel dichloride hydrates are stable over the following temperature ranges:

$\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$	low temperature
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	up to 36.25 °C
$\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$	36.25 to 75 °C
$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$	above 75 °C

The difluoride is only slightly soluble in water, but the other halides are very soluble (e.g., 117 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ per 100 mL solution at 20 °C).

Table 12.21: Nickel halides.

Compound	<i>d</i>	$-\Delta H^\circ$ (25 °C), kJ/mol	Color
NiF_2	4.63	651	light green
NiCl_2	3.55	305	pale yellow
NiBr_2	5.10	212	yellow
NiI_2	5.83	78	black
$\text{NiF}_2 \cdot 4\text{H}_2\text{O}$	2.22		light green
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	1.92	2103	green
$\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$		1146	yellow-green
$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$			blue-green

The difluoride has a tetragonal structure, and the other dihalides have hexagonal layer structures. They are relatively stable, and can be melted or sublimed in a vacuum or under an inert atmosphere.

Production. The anhydrous halides can be made by direct reaction of the elements at high temperature or in nonaqueous solution, although the fluoride is better made indirectly. They are also formed by dehydration of the hydrates in a stream of the hydrogen halide gas to prevent formation of nickel oxide.

The hydrates can be made by dissolving nickel metal, oxide, hydroxide, or carbonate in an aqueous solution of the halogen acid HX, followed by crystallization. Commercially, nickel dichloride hexahydrate is usually pro-

duced by dissolving nickel metal in hydrochloric acid, and then crystallizing. Nickel dichloride solutions are important in chloride-based processes for the extraction of nickel, but nickel metal is usually recovered by electrowinning.

Table 12.22: Specifications of nickel chloride hexahydrate for electroplating.

	BS 564 (1970), %	DIN 50970, %
Ni	24.0 (Ni + Co) min.	23.7 min.
Co	1 % of total metal, max.	0.5 max.
Cu	0.005 max.	0.002 max.
Fe	0.01 max.	0.01 max.
Pb	0.002 max.	0.002 max.
Zn	0.002 max.	0.006 max.
Insolubles	0.05 max.	0.05 max.
pH (40 % w/v)	2.0 min.	

Uses. Nickel dichloride hexahydrate is important in electroplating; it is used together with nickel sulfate in the Watts plating bath. Table 12.22 lists the purity specifications for its use in electroplating. It is also used in the production of some catalysts. Uses of the other dihalides are very minor.

Nickel(II) hydroxide, $\text{Ni}(\text{OH})_2$, *d* 4.15, ΔH° (25 °C) -514 kJ/mol. Treating a nickel salt solution with an alkali-metal hydroxide solution gives a green gelatinous precipitate of nickel hydroxide, also known as nickel hydrate. Filtering, washing, and drying give the pure compound. The precipitation conditions affect the physical characteristics of the nickel hydroxide produced.

Nickel hydroxide is virtually insoluble in water, but it is soluble in dilute acids, giving a nickel salt solution, and in ammoniacal solutions a blue ammine complex is formed. Heating to ca. 250 °C drives off water, leaving nickel oxide.

Nickel hydroxide has some use as an intermediate in catalyst production, but its main use is as the active mass in the positive electrode in nickel cadmium batteries. In pocket-plate electrodes, pellets of nickel hydroxide are used. In sintered electrodes, the nickel hydroxide is prepared within the electrode either by precipitation or electrochemically.

There are various hydrated oxides or hydroxides containing Ni(III) and possibly Ni(IV), some of which are not well characterized. The compounds are black and are referred to as nickel peroxide, nickelic hydroxide, or nickel black.

The β -NiO·OH, obtained by the oxidation of nickel salts in alkaline solution with an oxidizing agent such as sodium hypochlorite, is well characterized. It is also formed in batteries when Ni(II) hydroxide in a nickel electrode is charged.

Persulfate oxidation of nickel(II) hydroxide gives a substance formulated as NiO₂·xH₂O.

A commercial "nickel peroxide" corresponded to Ni₂O₃·2H₂O, and gave Ni₂O₃·H₂O (equivalent to NiO·OH) on partial dehydration [127].

Nickel(II) Nitrate. The commercially available compound is the green hexahydrate Ni(NO₃)₂·6H₂O, *d* 2.05, ΔH^0 (25 °C) -2212 kJ/mol. It is very soluble in water. On heating, the hexahydrate dissolves in its own water of crystallization at 56 °C. Progressive heating drives off the water of crystallization, giving basic nitrates and finally nickel(II) oxide.

The stability ranges of the hydrates are:

Ni(NO ₃) ₂ ·9H ₂ O	below -3 °C
Ni(NO ₃) ₂ ·6H ₂ O	-3 to 54 °C
Ni(NO ₃) ₂ ·4H ₂ O	54 to 85.4 °C
Ni(NO ₃) ₂ ·2H ₂ O	85.4 to ca. 105 °C

Nickel nitrate solution can be produced by dissolving nickel in nitric acid. The reaction is vigorous, and without careful control loss or breakdown of the nitric acid occurs, forming, among others, ammonium nitrate. The dissolution of nickel(II) oxide in nitric acid is easier to control; the hexahydrate is produced by crystallization of the resulting solution.

It is difficult to prepare the pale green, anhydrous nickel(II) nitrate by dehydration of the hexahydrate. It can be obtained by dehydration with dinitrogen pentoxide in fuming nitric acid, or from nickel tetracarbonyl and dinitrogen tetroxide.

Nickel(II) nitrate hexahydrate is widely used in the production of nickel catalysts, by impregnating an inert carrier and decomposing the nitrate. It is also used in the formation

of the nickel(II) hydroxide active mass in sintered nickel electrodes for nickel cadmium batteries.

Nickel(II) Oxide. Nickel oxide, NiO, *d* 6.8, ΔH^0 (25 °C) -240 kJ/mol, is green, with a cubic rock-salt structure. It occurs in nature as bunsenite. The exact color depends on factors such as purity and crystallite size. In general, the properties of nickel oxide depend on the method of preparation, especially temperature.

Nickel(II) oxide has a defect structure Ni_{1-y}O, which is responsible for its *p*-type semiconductor properties. In addition, nickel oxide can absorb surface oxygen to give higher O:Ni ratios. There is little evidence for Ni₂O₃ as a bulk compound, although it may exist as a surface compound on NiO.

World production of "nickel oxide" is ca. 40 000 t/a from INCO in Canada, Greenvalle in Australia, and from Cuba, but only about 4000 t of this is chemical nickel oxide. The majority is metallurgical nickel oxide, or partially reduced nickel oxide containing 85–90% nickel, used mainly in the stainless steel industry. Chemical nickel oxide is available in two forms: green or black.

Production. Green nickel oxide can be made by calcining almost any nickel compound in air, for example, the nitrate, oxalate or hydroxide, at ca. 1000 °C. It can also be made by oxidation of carbonyl nickel powder, but some care is needed to ensure complete oxidation.

Black, or soluble, nickel oxide is made by calcining basic nickel carbonate at ca. 550 °C; it contains a slight excess of oxygen.

The green oxide is rather refractory, and dissolves only slowly in mineral acids. The black oxide is more reactive and dissolves readily. Both forms are insoluble in water and are easily reduced, for example by hydrogen, to nickel metal.

Uses. Nickel oxide is used in the production of catalysts, in the enamel industry for making frit, in the glass and ceramics industries, and in the manufacture of ferrites for the electronics industry.

Black nickel oxide is particularly suitable for dissolving in acids as a first step in the production of specialty nickel salts.

Higher oxides such as Ni₂O₃, and NiO₂ have been proposed but there is little evidence for their existence free of water.

Nickel(II) Sulfate. Two forms of nickel(II) sulfate are commercially available. The most common is the blue-green, tetragonal hexahydrate α -NiSO₄·6H₂O, *d* 2.07, ΔH^0 (25 °C) -2683 kJ/mol, nickel content 22.3%, which crystallizes from solution between 30.7 and 53.8 °C. The other form is the green, orthorhombic heptahydrate NiSO₄·7H₂O, *d* 1.95, nickel content 20.9%, which crystallizes from solution below 30.7 °C. Crystallization above 53.8 °C gives green β -NiSO₄·6H₂O.

The hydrates are readily soluble in water. The solubilities in grams per liter of solution are (the temperature in °C is given in parentheses):

NiSO ₄ ·7H ₂ O	578 (10)
NiSO ₄ ·7H ₂ O	775 (30)
α -NiSO ₄ ·6H ₂ O	770 (40)
α -NiSO ₄ ·6H ₂ O	851 (50)
β -NiSO ₄ ·6H ₂ O	959 (60)
β -NiSO ₄ ·6H ₂ O	1258 (100)

Data also exist for the solubility of nickel sulfate in sulfuric acid [128].

Heating the hydrates causes dehydration. Hydrates with 4 or 1 molecule of water are stable. The bright yellow, cubic, anhydrous salt NiSO₄, *d* 3.68, ΔH^0 (25 °C) -873 kJ/mol, is obtained above 330 °C. This decomposes above ca. 800 °C to give nickel oxide and sulfur trioxide. The lower hydrates can also be obtained by crystallization from nickel sulfate solutions containing excess sulfuric acid. They dissolve only slowly in water. Basic sulfates also exist.

Production. The worldwide production capacity is about 40 000 t/a, from producers in Europe, Japan, China, and the former Soviet Union. Most of the nickel sulfate is a by-product of electrolytic copper refining. A bleed stream is purified, finally giving a solution from which nickel sulfate is crystallized.

Nickel sulfate is also produced by dissolving nickel or nickel oxide in sulfuric acid and crystallizing. Several nickel refineries produce

nickel sulfate solution by leaching nickel mattes with sulfuric acid, but the nickel is usually recovered as nickel metal by electrowinning.

Uses. The main use of nickel sulfate is as the electrolyte in nickel electroplating baths. Table 12.23 lists the standards covering nickel sulfate for use in electroplating. It is also used in electroless nickel plating, in catalyst manufacture, and in the production of other nickel compounds.

Nickel Sulfides. Nickel(II) sulfide, NiS, *d* 5.65, ΔH^0 (25 °C) -82 kJ/mol, *mp* 797 °C.

Neutral nickel(II) salt solutions react with ammonium sulfide initially to give black α -NiS, a hydrous, amorphous precipitate of the type Ni(SH,OH)₂. At low pH, this crystallizes to give rhombohedral γ -NiS, whereas in more alkaline solution hexagonal β -NiS is formed.

Table 12.23: Specifications of nickel sulfate hexa- or heptahydrate for electroplating.

	BS 564 (1970) (6 or 7 hydrate), %	DIN 50970 (6 hydrate), %
Ni + Co	20.7 min.	22.0 min.
Co	1 % of total metal, max.	0.5 max.
Cu	0.002 max.	0.002 max.
Fe	0.005 max.	0.005 max.
Pb	0.002 max.	0.002 max.
Zn	0.002 max.	0.006 max.
Cd		0.005 max.
As		0.001 max.
Insolubles	0.005 max.	0.005 max.
pH (40 % w/v)	2 min.	

The γ -form occurs in nature as millerite. This shows little deviation from stoichiometry, but a high-temperature form has a stoichiometry range.

Other nickel sulfides exist, some of which occur in nature. These are Ni₃S₂, Ni₇S₆, Ni₃S₄, and NiS₂. All can be prepared by fusing the correct proportions of the elements.

Sulfide minerals are a major source of nickel, and nickel sulfide is an important intermediate in refining processes. The main use of nickel sulfides is as catalysts, for example, in the hydrogenation of sulfur compounds. The catalyst can be prepared in situ by sulfiding a supported nickel catalyst.

Nickel(II) tetrafluoroborate, $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, can be made as apple green needles by reacting fluoroboric acid with basic nickel carbonate, and crystallizing from solution. It has limited use in specialty high-speed nickel plating process, and other minor uses.

Nickel Complexes. In common with all transition metals nickel forms a vast number of inorganic complexes with different oxidation states and geometries. Only the ammine complexes, which are important in ammonia-based leaching processes, have industrial significance.

The structural, spectral, and magnetic properties of nickel complexes are important in studies of transition-metal complex chemistry. In particular, there are concentration and temperature dependent anomalies in properties due to polymerization and equilibria between different geometries.

The most common complex ion is octahedral Ni(II) , for example, the green $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ in aqueous solution. The electronic structure of these complexes is $[\text{Ar}]3d^8$ with two unpaired electrons, and hence they are paramagnetic. Other species can displace water molecules, for example, ammonia molecules in ammine complexes $[\text{Ni}(\text{H}_2\text{O})_x(\text{NH}_3)_{6-x}]^{2+}$, $x = 0-6$, which are blue or purple. The complex ion $[\text{Ni}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$ is the required ion in solution for the production of nickel powder by pressure reduction of solutions by hydrogen.

Four-coordinate Ni(II) complexes are quite common, either diamagnetic square planar complexes such as the yellow $\text{Ni}(\text{CN})_4^{2-}$ or paramagnetic tetrahedral complexes such as NiCl_4^{2-} . Five-coordinate Ni(II) complexes also exist, and are either trigonal bipyramidal or square pyramidal.

Complexes of nickel in lower oxidation states are mostly based on carbonyl ligands. An example of Ni(0) is $\text{Ni}(\text{PF}_3)_4$ and of Ni(I) , $\text{Ni}(\text{PPh}_3)_3\text{X}$ ($\text{X} = \text{Cl, Br, I}$).

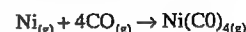
Higher oxidation states are stabilized by electronegative elements, e.g., Ni(III) in the violet K_3NiF_6 and Ni(IV) in red K_2NiF_6 , both of which are octahedral.

12.17.1 Nickel Tetracarbonyl

Nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, *bp* 42.2 °C, *mp* -19.3 °C, *d* 1.31, is a very toxic colorless liquid. It possesses a significant vapor pressure at ambient temperature (44 kPa at 20 °C; 65 kPa at 30 °C).

Nickel tetracarbonyl is virtually insoluble in water, but soluble in many organic solvents. It does not react with dilute mineral acids. It is thermally unstable, decomposing to nickel and carbon monoxide. It burns in air with a luminous flame, giving nickel oxide and carbon dioxide, and forms explosive mixtures with air (3–34 vol% $\text{Ni}(\text{CO})_4$). The molecule is tetrahedral, with linear Ni-C-O bonds. The bonding consists of both a $\text{Ni-C } \sigma$ -bond and π bonding.

Production. Nickel tetracarbonyl is formed by direct reaction of carbon monoxide and finely divided nickel at relatively low temperatures:



$$\Delta G = -160\,410 + 418.27T \text{ J/mol} [129]$$

At atmospheric pressure, the maximum rate of formation of nickel tetracarbonyl is at 130 °C for pure nickel. The temperature at which the rate of formation is a maximum decreases in the presence of a catalyst such as sulfur, and increases with pressure. The reverse reaction begins above ca. 180 °C. This reversible reaction is the basis of the atmospheric-pressure Mond process and the INCO pressure process for the production of high-purity nickel pellet and powder. Nickel tetracarbonyl can also be prepared in solution by a variety of methods [130]. Users of nickel tetracarbonyl frequently produce their own supply, but it is commercially available in the United States.

The conditions under which nickel tetracarbonyl is formed are important because of the possibility of corrosion or transfer of nickel within a system, and in view of its high toxicity. The mere coexistence of carbon monoxide and nickel in some form does not mean that nickel tetracarbonyl will form. Other criteria must be met:

- A fully reduced nickel-containing surface,
- A reducing gas containing carbon monoxide,
- The formation must be thermodynamically possible, which generally means low temperature (ambient to 150 °C) and high carbon monoxide partial pressures.

In addition, the presence of a catalyst such as sulfur accelerates nickel tetracarbonyl formation.

One situation where a significant amount of nickel tetracarbonyl can form is from a finely divided reduced nickel catalyst and carbon monoxide at low temperature. This is well known to users of nickel catalysts, and such conditions are avoided. Other than this, it is rare that significant amounts of nickel tetracarbonyl are formed. Environmentally, precautions preventing contamination of the workplace by the carbon monoxide will also prevent contamination by any nickel tetracarbonyl.

The presence of nickel tetracarbonyl has been suggested but not demonstrated in cigarette smoke and in gases from the combustion of fossil fuels containing nickel. Attempts to detect it in welding fume failed [131].

Uses. Apart from being an intermediate in the carbonyl refining of nickel, nickel tetracarbonyl can be thermally decomposed to nickel plate other materials, for example, in mold production or in a fluidized bed. It is also used as a carbonylating agent or catalyst in organic chemistry.

Analysis. Nickel tetracarbonyl can be analyzed by decomposition and conventional analysis of the nickel, by gas chromatography, UV or IR spectroscopy. There is a highly sensitive method based on the chemiluminescent reaction of nickel tetracarbonyl with ozone [132]. Commercial instruments based on infrared or chemiluminescent analysis are available.

Reactions of Nickel Tetracarbonyl. Nickel tetracarbonyl undergoes oxidation, reduction, and substitution reactions [133, 134]. These are normally carried out in organic solvents

below ca. 50 °C to prevent thermal decomposition of the nickel tetracarbonyl.

Reaction with various oxidizing agents gives Ni(II) compounds. Concentrated nitric acid gives nickel nitrate. Solutions of nickel tetracarbonyl in organic solvents are oxidized by air to basic nickel carbonate and by halogens to the corresponding nickel dihalide. Decomposition of nickel tetracarbonyl with bromine water is useful as a means of disposal or for analysis.

Reduction reactions, generally with alkali metals, give polynuclear anions formulated as $[\text{Ni}_2(\text{CO})_6]^{2-}$, $[\text{Ni}_3(\text{CO})_8]^{2-}$, $[\text{Ni}_4(\text{CO})_9]^{2-}$, $[\text{Ni}_5(\text{CO})_9]^{2-}$, and $[\text{Ni}_6(\text{CO})_{12}]^{2-}$. Reduction of nickel tetracarbonyl by alkali metals in liquid ammonia gives a carbonyl hydride $[\text{NiH}(\text{CO})_3]_2$, isolated as a tetraammoniate.

Interest in substitution compounds of nickel tetracarbonyl blossomed following the publication in 1948 of work by REPPE and co-workers showing that an effective class of catalysts for the trimerization of acetylene compounds could be formed by substituting CO groups in $\text{Ni}(\text{CO})_4$ by donor ligands such as triphenylphosphine.

Thousands of substitution compounds of nickel tetracarbonyl have now been prepared. Most are with ligands containing the group 15 elements phosphorus, arsenic, or antimony as electron donor, but carbon, nitrogen, and unsaturated organic molecules can also serve as ligands.

Some of the simpler substitution compounds with phosphorus ligands are $\text{Ni}(\text{CO})_n(\text{PX}_3)_{4-n}$, $n = 0-3$, $\text{X} = \text{H, F, Cl, CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$ (substituted phosphines) and $\text{X} = \text{OCH}_3, \text{OC}_2\text{H}_5, \text{OC}_6\text{H}_5$ (phosphites). The degree of substitution is controlled by steric and electronic effects. For example, with PF_3 and $\text{P}(\text{C}_6\text{H}_5)_3$, only mono- and disubstituted compounds are formed, whereas with PCl_3 and $\text{P}(\text{OC}_6\text{H}_5)_3$ the carbon monoxide molecules can be completely replaced. The tetrakis(ligand) compounds $\text{Ni}(\text{PF}_3)_4$ and $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ can be prepared by other means. Substitution by chelating ligands is also possible, e.g., $(\text{CO})_2\text{NiL}'$ and NiL'_2 , where $\text{L}' = o\text{-C}_6\text{H}_4[\text{P}(\text{C}_2\text{H}_5)_2]_2$.

Fewer substitution compounds based on arsenic and antimony have been prepared. Examples include $\text{Ni}(\text{CO})_3\text{AsX}_3$ ($\text{X} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{OC}_6\text{H}_5$) and $\text{Ni}(\text{CO})_3\text{SbX}_3$ ($\text{X} = \text{Cl}, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{OC}_6\text{H}_5$).

12.17.2 Nickel Salts of Organic Acids

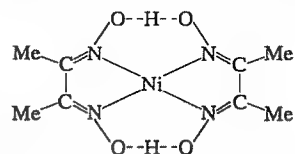
Nickel(II) acetate tetrahydrate $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, d 1.744, can be obtained as green crystals when solutions of nickel(II) hydroxide or carbonate in acetic acid are evaporated at room temperature. It is readily soluble in water but is insoluble in ethanol.

Anhydrous nickel(II) acetate $\text{Ni}(\text{CH}_3\text{COO})_2$, d 1.798, can be prepared by dehydration of the tetrahydrate in vacuum or by heating the tetrahydrate under reflux with acetic anhydride. When heated in the absence of air these acetates decompose to give a residue of nickel and Ni_3C , evolving, among other products, carbon monoxide and carbon dioxide. Nickel acetate is a suspect carcinogen: the LD_{50} (rat) is 350 mg/kg [135].

Nickel(II) acetylacetonate $\text{Ni}(\text{CH}_3\text{COCHCOCH}_3)_2$, mp 230 °C (dec.), is obtained as emerald green crystals by dehydration of the dihydrate at 50 °C in vacuum; it has an unusual trimeric structure in the solid state [136]. The dihydrate $\text{Ni}(\text{CH}_3\text{COCH}_3)_2 \cdot 2\text{H}_2\text{O}$ is prepared by the addition of acetylacetone to solutions of nickel(II) salts in the presence of a weak base such as sodium acetate. Nickel(II) acetylacetonate is soluble in organic solvents and finds use in the synthesis of organometallic compounds such as nickelocene and bis(cyclooctadiene) nickel. It is also industrially important as a catalyst component in the oligomerization of alkenes and in the conversion of acetylene to cyclooctatetraene [137, 138].

Nickel(II) dimethylglyoximate bis(dimethylglyoximate) nickel(II), $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$, is obtained quantitatively as a bright red precipitate when an alcoholic solution of dimethylglyoxime is added to a neutral or slightly

alkaline solution of a nickel(II) salt. This reaction is used in the gravimetric estimation of nickel [139] and is also useful as a spot test for the presence of nickel ions. The structure of this diamagnetic solid [139] shows the nickel(II) ion to be in a square-planar environment; the dotted lines represent strong intramolecular hydrogen bonds.



Nickel(II) formate dihydrate $\text{Ni}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, d 2.154, is obtained as green crystals by evaporation of a solution of nickel carbonate in formic acid. The anhydrous salt is obtained when the dihydrate is heated to 140 °C; at 250 °C, finely divided nickel metal is produced. Hence, nickel(II) formate is used in the production of nickel catalysts.

Nickel(II) oxalate dihydrate $\text{Ni}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$, precipitates as a green powder when oxalic acid or alkali-metal oxalate solutions are added to nickel(II) salt solutions. When heated in vacuum, it evolves water at 150 °C and decomposes completely at 300 °C, giving finely divided nickel suitable for use in catalysis or in the production of nickel carbonyl.

12.17.3 Analysis

The classical analytical method for nickel in solution is gravimetric, by precipitation of the red complex with butanedione dioxime (dimethylglyoxime). Other methods include electrodeposition, EDTA titration, and the standard spectroscopic methods of atomic absorption, flame emission, inductively coupled plasma optical emission, and X-ray fluorescence. There is a standard analytical method for nickel in biological tissue [140].

12.17.4 Economic Aspects

In general, nickel compounds cost the London Metal Exchange (LME) price for the contained nickel, plus a premium based on the

production cost. However, companies producing nickel compounds, particularly nickel sulfate, as a by-product of other processes are more flexible in their pricing.

The LME three-month nickel price decreased during the first part of the 1980s from about \$3 per pound in 1980 to below \$2 per pound in 1986. The price then rose to over \$5.50 per pound in 1988, but has since decreased.

12.17.5 Toxicology

12.17.5.1 Distribution in the Environment

Nickel is contained as a trace element in the soil in the lattices of iron and aluminum silicates, and the content is inversely proportional to the silicic acid content. At 40% or less of SiO_2 in the soil there is ca. 1600 g Ni/t while at 80% or more it is only 3 g Ni/t [141]. Nickel contents of 1–5 μg Ni/L are generally found in surface waters, but values as high as 264 μg Ni/L have been recorded. Plants generally contain 0.3–4 mg Ni/kg, and animals 0.1–3 mg Ni/kg (both dry weight). Atmospheric nickel in the United States averages 6 ng Ni/ m^3 (nonurban) and 20 ng Ni/ m^3 (urban), while 15.8 ng Ni/ m^3 has been observed near primary sources [142]. The major part is in the form of sulfates and oxides and results from burning of fossil fuels and industrial activity [143].

Ingestion. The normal Western diet contains 150–600 μg Ni/d, derived primarily from its being a natural trace constituent of many food stuffs (e.g., cocoa contains 9800 μg Ni/kg) [144] and secondarily during food processing, which frequently involves nickel-containing equipment. Although no specific function for nickel has been established in animals, dietary induced nickel deficiency has been observed experimentally [145].

12.17.5.2 Ecotoxicity

Plant Life. Nickel is an essential element for certain types of plant, for example, legumes. Nickel-tolerant plants with nickel contents up to 1.35% dry weight occur in some serpentine soils, and hyperaccumulators indicate nickel-rich soils. Nickel is also toxic to plant life; the effective dose that produces a 50% reduction in normal growth depends upon the species (e.g., for rye grass it is 0.18 ppm and for alfalfa, 5 ppm) [146]. Sewage sludge containing a high level of nickel can be harmful when spread on soil because of the persistence of the metal and the difficulty of its removal.

Aquatic Toxicity. Results of acute toxicity tests depend upon the aquatic species, test conditions, and the solubility of the nickel compound under test. For example the LC_{50} for rainbow trout at a water hardness of 100 mg/L is 0.05 mg Ni/L [147].

12.17.5.3 Mammalian Toxicology

Human Carcinogenesis. The first suspicion that nickel might cause respiratory cancer followed the occurrence of a nasal cancer in a Welsh refinery worker in 1923 [148]. Subsequent observations of excess nasal and pulmonary cancers at this and other refineries (in Ontario, Canada; Kristiansand, Norway; and the former Soviet Union) resulted in suspicion falling on the high-temperature roasting of nickel-copper matte or impure nickel subsulfide or on nickel oxide, but there was no supporting evidence of any similar risk in other refining operations or in the nickel-using industries. This subject has been extensively reviewed by the International Committee on Nickel Carcinogenesis in Man, (ICNCM) [149], which updated the existing studies and evaluated the collective results. Exposures to high levels of sulfidic and oxidic nickel (especially nickel subsulfide and nickel copper oxide) were found to be implicated as well as impure soluble nickel compounds such as nickel sulfate in the Norwegian and Welsh refineries. However, at each facility where nickel sulfate exposure was associated with

excess cancer, there were also exposures to other substances. The ICNCM concluded that more than one form of nickel gave rise to respiratory cancer in men employed at the refineries considered in the study and "the respiratory cancer risks were primarily related to exposure to soluble nickel at concentrations in excess of 1 mg Ni/m³ and to less soluble forms at concentrations greater than 10 mg Ni/m³". The ICNCM found that:

- There was an absence of any evidence of hazard from metallic nickel,
- There was no substantial evidence that occupational exposure to nickel or any of its compounds was likely to produce cancer other than in the lung or nose,
- The few small excesses that were observed in cohorts with excess lung or nasal cancer could be attributed to misdiagnoses (bone and pharynx) or to chance (prostate).

The group also considered that the risk to the general population from exposure to < 1 µg Ni/m³, in the ambient air, is minute or non-existent.

Experimental Carcinogenesis. Experiments have been carried out in vivo and in vitro to establish the carcinogenicity of nickel and its compounds. A variety of routes of administration and animal species have been involved. The National Toxicological Programme in the United States is currently conducting a major inhalation bioassay on rodents, using nickel subsulfide, nickel oxide, and nickel sulfate [150]. Existing studies have been extensively reviewed [151–155]. An IARC review and assessment was published in 1990 [156]. SUNDERMAN [157] suggested that the ability of nickel to enter the target cell and release ions is the major determinant in carcinogenicity. This may occur by endocytosis, transmembrane diffusion, or the Ca²⁺ transport route. Having reached the target tissue the nickel ion may act by:

- Direct genotoxic mechanisms,
- Tumor promotion by blocking cell-to-cell communications,

- Enhancing tumor progression by inhibiting natural killer cell activity.

These processes can be modified by manganese and magnesium. Toxicity is related partly to the concentration of nickel reaching the intracellular tissues but also to the ability of cells to phagocytose less soluble particles.

Species Specific Carcinogenesis. Nickel subsulfide has been shown to be highly carcinogenic to rats by injection into a variety of tissues [158]. There is also a single positive inhalation study [159] and a dose-related positive intratracheal study in female rats [160]. The crystalline form was positive in in vitro tests [161]. There is some evidence of mutagenic potential of nickel sulfide in vitro but not in vivo [152].

The data for *nickel oxide* are less clear cut. The biological activity of nickel oxide is related to the temperature of its formation [154]; nevertheless, an inhalation study with high exposures (53.2 mg/m³) to the more reactive black form failed to produce a carcinogenic response [162]. Cell transformation studies with nickel oxide have given marginally weak positive results [152].

Metallic nickel dust has come under suspicion as an animal carcinogen but to date no adequate inhalation data have been produced [151]. Using intratracheal and intraperitoneal injections of metallic nickel powder, as well as a variety of nickel compounds and nickel alloys in female rats, POTT and coworkers [160, 163] obtained positive results, but intratracheal instillation of nickel metal and alloys in hamsters was negative [164].

The carcinogenicity of soluble nickel salts has also been studied and is currently of particular interest in view of the findings of the ICNCM [149]. In vitro studies involving nickel sulfate proved negative in the Syrian hamster embryo test but positive in cell transformation assays [165].

Allergenicity. Nickel contact dermatitis is a well recognized clinical entity [166]. In Denmark, 10% of women and 2% of men are known to be sensitized and similar results have come from elsewhere. Sensitization is

due to nickel-containing articles coming into contact with the skin. Persons who are sensitized can exhibit local or general cutaneous reactions. These can arise from external contact and may be exacerbated by internal exposure to nickel in food or prosthetic devices. Persistent hand eczema may occur. Recent studies have indicated that sensitization can be avoided by the use of alloys that are resistant to corrosion by sweat, and legislation has been effected in Denmark to eliminate the use of leachable alloys next to the skin (Decree 88/0088DK). Primary nonallergic skin irritation may occur from the handling of solutions of soluble nickel salts as in plating.

Pulmonary sensitization has occurred in a few workers exposed to aerosols of soluble nickel salts, generally the sulfate [132], which may also cause nasal irritation and epistaxis.

Acute Poisoning. Insoluble nickel is very poorly absorbed through the gastrointestinal tract and its toxicity is therefore low (Table 12.24) [167]. Human experience with soluble salts consists of death in a child who ate 5 g of nickel sulfate [152] and illness lasting a few days in workers who accidentally drank water contaminated with 1.63 g/L of soluble nickel (total dose of 0.5–2.5 g Ni) [168].

Table 12.24: Acute toxicity of nickel compounds in Sprague-Dawley rats, mg/kg [167].

Substance	LD ₅₀ , male	LD ₅₀ , female	Combined response	
			LD ₅₀	CI ^a
NiCl ₂ ·6H ₂ O	210	175	200	186–214
NiO, black, acid soluble	> 5000	> 5000	> 5000	
NiO, green, high temperature	> 5000	> 5000	> 5000	
Nickel powder	> 9000	> 9000	> 9000	
Ni ₃ S ₂	> 5000	> 5000	> 5000	
NiSO ₄ ·6H ₂ O	325	275	300	201–399
Ferronickel (30% Ni)	> 5000	> 5000	> 5000	
Ni(OH) ₂	1500	1700	1600	1176–2024
NiS, amorphous	> 5000	> 5000	> 5000	
NiCO ₃ ·xH ₂ O	1305	840	1044	822–1281
Ni(NH ₄) ₂ (SO ₄) ₂	440	400	420	340–1281
Ni ₃ As ₂	5840	6800	6300	5140–7470

^a CI = 95% Confidence interval.

Chronic Pulmonary Changes. Very high exposure to dust containing nickel oxide resulted in pneumoconiosis in hamsters. Lower exposures to soluble nickel and nickel metal powder caused injury to lung tissue at the macro- and microscopic levels. No clear evidence has been produced to suggest that pneumoconiosis or chronic bronchitis result from human exposure [132]. Nickel sulfate has also been shown to cause inflammatory reactions in lung tissue and olfactory epithelium in rats at concentrations of ca. 0.1 mg Ni/m³ [169].

12.17.5.4 Nickel Carbonyl Poisoning

Acute Poisoning. Exposure to nickel carbonyl gas is most likely to occur in accidental situations at refineries using the carbonyl process or in research laboratories. Accidents have occurred when carbon monoxide was passed over reduced, finely divided nickel at ambient temperature in catalyst manufacture and in some plating operations.

Poisoning by nickel carbonyl is characterized by a two-stage illness. The first consists of headaches, malaise, and pain in the chest lasting a few hours; this is generally followed by a short remission. The second phase starts after ca. 16 h. Symptoms of cough, breathlessness, and extreme fatigue characterize this chemical pneumonitis, which reaches its greatest severity in about four days. Death may result from cardiorespiratory or renal failure. Convalescence is often extremely protracted and is often complicated by depression, exhaustion, and dyspnea on exertion. Permanent respiratory damage is unusual. The severity of an exposure is established by the clinical findings and by monitoring urinary nickel [170]. Oxygen therapy in the early stages reduces the severity of any pulmonary edema. Sodium diethyldithiocarbamate chelates nickel and is used as a therapeutic agent. In practice its biological analogue, disulfiram (Antabuse) is more readily available and is an effective drug. Treatment (250 mg–1 g) should be started as soon as possible after exposure and accompanied by in-

haled and systemic steroids in order to minimize pulmonary toxic reactions [171]. Oxygen therapy may be indicated.

Carcinogenicity. There is debate about the carcinogenicity of nickel carbonyl gas [172]. However, since in modern refineries ambient levels are maintained below the local limit of detection (Section 12.17.5.5) in order to avoid acute effects, such debate is of no practical significance. Furthermore, epidemiological

data from the Clydach Refinery indicate that the cancer risk there was associated with the exposure to dust involved in the refining process rather than nickel carbonyl [173].

Teratogenicity. SUNDERMAN exposed rats to nickel carbonyl early in pregnancy and 28% were born with ocular abnormalities [174]. No similar effect has been noted with other nickel compounds.

Table 12.25: Labelling, limit values and legislation for nickel. Numbers within braces refer to notes following in the text.

	EC directives	EC member states (special rules)	United States	Canada
Occupational exposure limit	No figures yet; however, note directive 88/C34/03 ⁽¹¹⁾	Germany ⁽²⁾ 0.5 UK ⁽³⁾ 0.5 France 0.5 1 ⁽⁴⁾ 0.05 0.1 0.1 0.007 ^(4,5)	1 ⁽⁴⁾ 0.1 ⁽⁴⁾ 0.3 0.007 ^(4,5)	e.g., Ontario ⁽⁶⁾ 1 0.1 0.35
General Atmospheric Emission	Air pollution from industrial plants; EC 84/360 ⁽⁷⁾	TALuft 1 mg/m ³ ⁽¹⁸⁾ UK 5 mg/m ³ ⁽¹⁹⁾	Nil specific ⁽¹⁰⁾	e.g., Ontario ⁽¹¹⁾ 5 µg/m ³
Level in drinking water ⁽¹²⁾	EC 80/778 ⁽¹³⁾ 50 µg/L	Applicable throughout EC ⁽¹⁴⁾	Guidance limit 0.15–1 mg/L SDWA 1986 ⁽¹⁵⁾	CWQG ⁽¹⁶⁾
Effluent discharge ⁽¹⁷⁾	EC 76/464 8–100 µg Ni/L ⁽¹⁸⁾ Sewage sludge EC 86/278 ⁽¹⁹⁾	UK The Red List, local consent 5.0 mg/L ⁽²⁰⁾ Germany 0.3 mg/L	Site consents daily max. 3.98 mg/L CWA ⁽²¹⁾	0.5 mg/L ⁽²²⁾ 1 mg/L ⁽²³⁾
Labelling requirements and subsequent amendments	EC 67/548 ⁽²⁴⁾ 79/831 83/467 90/C33/03	Germany Nickel powder and some insoluble Ni compounds require "cancer" label for inhalable forms ⁽²⁵⁾	Yes HCR 29CFR 7 ⁽²⁶⁾	Yes WHIMIS ⁽²⁷⁾
Importing and shipping rules	International rules IMDG Code 25A ⁽²⁸⁾ ADR (Road) ⁽²⁹⁾ Hazardous waste 86/279 ⁽³⁰⁾	Applicable throughout EC	TSCA Includes Ni ⁽³¹⁾ Dept. of Trade Regulations	Transport of Dangerous Goods Act IMDG Code
Industrial disease compensation	Commission recommendation 90/326/EC	UK Social Security Act Nickel refining 22a&b Nickel carbonyl C14 ⁽³²⁾ France = Matte roasting ⁽³³⁾	Workers Compensation & Common Law	Each province has specific Workers Compensation Acts
Emergency planning and right to know	Directive EC 82/501 amended; trigger at 1 t of Ni oxides, sulfides, and carbonates present as powders ⁽³⁴⁾	Applicable throughout EC	Superfund and right to know; nickel listed ⁽³⁵⁾ NIEHS 1989 report ⁽³⁶⁾	No right to know requirements

Notes for Table 12.25:

1. Directive 88/C34/03 (Carcinogens) relates to certain nickel refining processes.
2. MAK: Maximale Arbeitsplatzkonzentrationen 1989. In Germany preventive measures have to be taken at action levels below these limits.
3. EH 40/90 of the Health & Safety Executive. These are maximum values and it is necessary to get as far below them as it is reasonably practicable. For Ni(CO)₄ this is a 10 min short-term exposure limit.

4. OSHA Permissible Exposure Limits 29CFR (1910.1000).
5. ACGIH (American Conference of Governmental Industrial Hygienists) propose reduction of Threshold Limit Values (TLVs) to 0.05 mg/m³.
6. ACGIH figures generally used in Canada, the provinces make own rules.
7. Directive 84/360 (Air Pollution from Industrial Plants).

8. German regulations Technische Anleitung zur Reinhaltung der Luft (TA Luft of 27. February 1986) applicable to Belgium and Holland.
9. Notice on best practical means; Jan. 1988.
10. Environmental Protection Agency — nil specific for Nickel, some states have specific levels.
11. Ontario Environmental Pollution Act. Regulation 308 Schedule 1 (half hour average).
12. Sayre I. M. International Standards for Drinking Water J. American Water Works Association 80(1):53–60 January 1988.
13. Directive 80/778 Drinking Water Directive.
14. United Kingdom Control of Pollution Act 1974 Part II.
15. Safe drinking water regulations 1986 Amendments. No standard set yet — guidance only.
16. Canadian water quality guidelines. Canadian Council of Resource & Environment March 1987.
17. Technical Report of Environmental Aspects of the Metal Finishing Industry, p. 53–57.
18. Nickel is a Class II material requiring legislation. Member states to make their own rules. Directive 76/464 (Pollution to the Aquatic Environment).
19. Directive 86/278 (environment, soil, sewage sludge) limits nickel in soil to 30–75 mg/kg and in sewage sludge to 300–400 mg/kg.
20. Water and the Environment DOE circular 7/89 of 30.3.1989.
21. Clean Water Act (Public Law 92-217) 1977.
22. Canadian Fisheries Act: Metal mining liquid effluent regulations.
23. Control of Industrial Water Discharge; Ontario.
24. Directive 67/548 (Classification packaging and labelling) has many amendments: the 7th is near adoption.
25. UK Classification, Packaging and Labelling of Dangerous Substances Regulations 1978. Similar rules in all European states. FRG Gefahrstoffverordnung: Inhalable nickel powder "may cause cancer".
26. Hazard Communication rule 29CFR7. Title 49 Transportation — Rules for packaging of Ni Powder.
27. Workplace Hazardous Materials Information System (WHIMIS).
28. International Marine Dangerous Goods Code.
29. European Agreement of International Carriage of Dangerous Goods by Road. HMSO 1985.21.
30. Directive 86/279. Transfrontier shipment of hazardous waste — amended 89/C9/01.
31. Toxic Substances Control Act TSCA. Nickel and many of its compounds are subject to TSCA and Section 5 requires the importer to comply with special rules and orders.

32. UK Social Security Act 1945. Industrial Diseases.
33. France: Tableaux de maladies professionnelles 37, 37 bis et 37 ter — 1987.
34. Directive 82/501 (Major Accident Hazards) amended as 88/C119/02. One tonne of nickel etc. in the form capable of causing a major accident hazard.
35. Title III Superfund amendments and reauthorisation Act (SARA); nickel listed in Section 3.13.
36. National Institute of Environmental Health Sciences 5th Annual Report on Carcinogens Summary 1989 NTP 89-239 Nickel pp. 187–192 (Legislation p. 192).
XX Others relevant EEC Directives with bearing upon nickel included are Major Accident Hazard and Amendments 88/610.
Protection of Water from Dusts related to Chemicals, Physical and Biological Agents at Work 88/842.

12.17.5.5 Legislation

Prevention of cancer in nickel workers is directed at maintaining occupational exposure as low as is reasonably practicable. This is achieved by the standard hierarchy of control measures: enclosure, wet methods of handling, exhaust ventilation, respiratory protection, and atmospheric monitoring. Biological monitoring is considered to be of little value [175].

Table 12.25 lists various legislative controls and where appropriate the relevant limit values. The notes attached to this table give the relevant authority.

Nickel is currently the subject of legislative activity in the EC and member states and also in the United States and considerable revision of these rules and limit values is likely to take place within the foreseeable future. The Directorate General XI (DGXI) of the EC is currently deciding on classification of pure substances. DGIII has responsibility for mixtures including alloys while DGV is involved in workplace safety and occupational exposure limits. In the United States the EPA is setting standards for nickel in the general atmosphere and water, and the ACGIH has proposed reduction of the TLV to 50 µg Ni/m³.

12.18 References

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Part Four

Secondary Metals

																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	Al											Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La [†]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac [‡]															

†	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
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‡	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
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13 Arsenic

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13.1 Introduction

Arsenic belongs to main group V of the periodic table and has an atomic number of 33. In compounds, it has oxidation states of 3+, 5+, and 3–.

Arsenic is a bright silver-gray metal. Its surface tarnishes in humid air. Arsenic forms trigonal crystals, which are brittle and of average hardness (3–4 on the Mohs scale).

In addition to the metallic modification, there are other modifications, namely, yellow arsenic and three amorphous forms (β , γ , δ) [1]. Of these, black arsenic (the β form) is the best known. Black arsenic is formed as a coating (arsenic mirror) when arsenic hydride is passed through an incandescent glass tube and also, together with other modifications, when the vapor is rapidly cooled. Yellow arsenic is formed by the sudden cooling of arsenic vapor and consists of transparent, waxy, regular crystals. It is unstable and changes into metallic arsenic on exposure to light or on gentle heating. All amorphous modifications change into the metallic form above 270 °C. Another form, brown arsenic (ρ 3.7–4.1 g/cm³), is either a special modification or simply a more finely divided form. This brown modification is obtained in the reduction of solutions of ar-

senic trioxide in hydrochloric acid with tin(II) chloride or hypophosphorous acid.

13.2 History

The natural sulfides, realgar and orpiment, were known in pre-Christian times and had already been named by ARISTOTLES and his pupil THEOPHRAST. In the first century A.D., PLINIUS mentioned sandarac (realgar) as occurring in gold and silver mines. The color of the yellow sulfide gave it the name orpiment. The Greek name $\alpha\rho\sigma\epsilon\nu\iota\kappa\omicron\nu$ (fearless, brave, manly), which was given to the sulfides on account of their reactivity with metals, derived from the custom prevailing at the time of classifying the metals as male or female. Subsequently, the name was applied to the metal itself. Many early authors described medicinal applications. DIOSKORIDES (first century A.D.) reported on the roasting of the sulfides and that they were used as remedies and artist's colors. In the fifth century A.D., OLYMPIODORUS described the production of the arsenic oxide As_2O_3 . An incomplete description of metallic arsenic dating from the fourth century has also been found. The alchemists were more closely concerned with the sulfides of arsenic. They generally called the roasted product "white arsenic". Many considered the arsenic oxide,

like sulfur, to be a basic constituent of metals. ALBERTUS MAGNUS apparently obtained the element in 1250; SCHRÖDER described two methods of preparation in 1649. In 1733, BRANDT showed that white arsenic is the oxide of the metal. The alchemists were aware of the poisonousness of white arsenic (As_2O_3). Records show that the compounds of arsenic were extensively used by the poison brewers of the Middle Ages. In the Renaissance it was PARACELSUS who pioneered the use of arsenic compounds in medicine. Arsenic acid and arsenic hydride were discovered by SCHEELE in 1775.

13.3 Physical and Chemical Properties

Densities: metallic arsenic 5.72 g/cm^3 at 20°C , yellow arsenic 2.03 g/cm^3

Melting point: 1090 K (817°C) at 3.7 MPa

Sublimation point: 886 K (613°C) at 0.1 MPa

Linear coefficient of thermal expansion: ca. $5 \times 10^{-6} \text{ K}^{-1}$

Specific heat capacity: $0.329 \text{ J g}^{-1} \text{ K}^{-1}$ at 291 K (18°C),

$0.344 \text{ J g}^{-1} \text{ K}^{-1}$ on average between 273 K (0°C) and 373 K (100°C)

Electrical resistivity: $24 \times 10^{-6} \Omega \cdot \text{cm}$ at 273 K (0°C)

The normal potential of arsenic with respect to the normal hydrogen electrode is ca. 0.24 V . Arsenic therefore comes between bismuth and copper in the electrochemical series.

The various forms of arsenic have different behaviors in air. Whereas the amorphous forms remain unchanged for months in dry air, the crystallized α form turns black in a few days, as originally observed by BERZELIUS. Powdered, moist arsenic is oxidized to arsenic trioxide with evolution of heat. When heated in air, it burns with a bluish-white flame, forming dense vapors of arsenic trioxide. When heated, arsenic metal gives off a characteristic garlic-like odor.

Concentrated nitric acid and aqua regia oxidize arsenic to arsenic acid; arsenic is oxidized to the 3+ state by dilute nitric acid or concentrated sulfuric acid and by boiling alkali hydroxides in air. Hydrochloric acid has little effect on arsenic. Chlorine combines fierily with arsenic to form arsenic trichloride. When the metal is heated with sulfur, AsS , As_2S_3 , or

As_2S_5 is obtained, depending on the ratios used. A mixture of fine arsenic and potassium chlorate explodes on impact.

Arsenic combines with metals to form arsenides. When subjected to oxidizing roasting, arsenides give partly metal oxide and arsenous acid and partly basic arsenates. When subjected to chloridizing roasting, they give arsenic trichloride. On heating in the absence of air, a sublimate of arsenic metal is formed from the heavy metal arsenides, although the arsenic can only be partly removed even at very high temperatures.

With oxygen, arsenic forms three oxides, namely arsenic trioxide, As_2O_3 ; arsenic pentoxide, As_2O_5 ; and As_2O_4 , which apparently contains trivalent and pentavalent arsenic alongside. The first two oxides may be regarded as acid anhydrides. Arsenous acid is derived from arsenic trioxide and can only exist in aqueous solution. Its well-known salts are the arsenates(III) (formerly arsenites). Arsenic acid is derived from arsenic pentoxide. Its salts, the arsenates, generally correspond to the phosphates in their stoichiometry. However, solid arsenic acids that correspond to the phosphorus acids are not known; instead, $\text{H}_3\text{AsO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ or $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ crystallizes from arsenic acid solutions.

The highly poisonous arsenic hydride, AsH_3 , is formed from arsenic compounds in acidic solution in the presence of strong reducing agents (e.g., Zn) or from suitable arsenides (e.g., As_2Zn_3) and acids.

13.4 Occurrence

Arsenic is widespread and can be detected in traces everywhere. Its abundance in the earth's crust is ca. $6 \times 10^{-4}\%$, i.e., it is roughly as abundant as molybdenum or tin, although the arsenic content of minerals is usually too low for them to have any economic significance.

Native arsenic is found in many places, but only in small quantities, usually in ores containing gold, silver, cobalt, nickel, and antimony. Although many arsenic-bearing

minerals are known, only a few occur in such quantities that they can be worked economically. The most important arsenic minerals are shown in Table 13.1. Other arsenides are chloanthite, NiAs_2 ; niccolite, NiAs ; smaltite, CoAs_2 ; cobaltite, CoAsS ; gersdorffite, NiAsS . Arsenic-bearing fahlores include inter alia tennantite, $4\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$; proustite, $3\text{Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$. These minerals may be regarded as thioarsenites. Enargite, $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5 = \text{Cu}_3\text{AsS}_4$, is a thioarsenate.

Table 13.1: Most important arsenic-bearing minerals.

	Mohs hardness	ρ , g/cm ³	Crystal system	Arsenic content, %
Arsenopyrite (FeAsS)	5.5–6	5.9–6.2	orthorh.	46
Löllingite (FeAs_2)	5–5.5	7.1–7.3	orthorh.	73
Orpiment (As_2S_3)	1.5–2	3.4–3.5	mon.	61
Realgar (AsS)	1.5–2	3.4–3.6	mon.	70
Native arsenic	3–4	5.6–5.8	trig.	90–100

13.5 Production

Most of the arsenic produced commercially accumulates as a by-product in the smelting of nonferrous metal ores containing gold, silver, lead, nickel, and cobalt.

Arsenopyrite often contains primary gold deposits. Fahlores and proustites always contain silver. Gersdorffite can accompany copper ores. Arsenopyrite and löllingite accompany pyrites [2].

Arsenic is mainly obtained from complex ores, such as enargite-containing copper, lead, and zinc ores and pyritic copper ores rich in arsenic. The arsenic content varies considerably.

Because of the volatility of arsenic sulfides and arsenic oxides, arsenic is concentrated in the gas phase. A crude oxide is produced from the intermediate products, and, after refining, is reduced to the metal or is sold as is to the chemical industry for further treatment.

The falling world demand for arsenic oxide, the increasingly elaborate treatment of complex ores, the high toxicity, and new environmental requirements have made arsenic-containing by-products a problem for many

producers. Recently, new methods have been sought to concentrate arsenic into more stable compounds or to avoid intermediate products altogether. Today arsenic is almost always an unwanted accompanying element in metallurgy.

13.5.1 Production of Arsenic Trioxide

History. Arsenic trioxide has been produced in China for 500 years in extremely simple plants, consisting of retorts with condensation chambers, from an ore containing 15% As. However, it was not until the beginning of the 18th century that a smelter for native arsenic was set up in Germany at the instigation of J. v. SCHARFENBERG in Reichenstein, Silesia. Because the demand for As_2O_3 was relatively low, it was not until the 19th century that a second country, Great Britain, began producing As_2O_3 . Thereafter, from the middle of the 19th century to 1901, Great Britain was the leading As_2O_3 producer. Production figures up to 1945 are only estimates. When legislation was introduced in various countries to avoid damage caused by release of As_2O_3 -containing fumes, world production of As_2O_3 increased considerably. The production of native arsenic was given a fresh impetus by the appearance of the boll weevil in Mexico and the United States – damage from 1909 to 1923 was estimated at \$3 billion. Calcium arsenate was used to combat the boll weevil. The demand for arsenic became so great that it exceeded supply. New plants were established, particularly in the United States and Mexico. The largest plant was operated between 1932 and 1962 by Boliden AB in Rönnskär, Sweden.

13.5.1.1 Beneficiation

The mining and dressing of ores with the primary object of recovering arsenic minerals are of little if any importance. Most arsenic raw materials are by-products from the dressing and smelting of arsenical ores. The raw materials differ widely in character: mostly

they are sulfides, often with pyrites as the principal constituent. For dressing, mixed arsenide-sulfide concentrates of very high metal content are floated, whereas the concentration of pure arsenic minerals is of secondary importance and should be avoided altogether.

The NF-metal concentrates used for the recovery of arsenic have arsenic contents from < 1% to, in exceptional cases, 10%. Table 13.2 shows As distributions in the concentrates and in the waste products, based on the As initial concentration in the ore.

In the concentration of complex ores, most of the arsenic remains in the tailings. In dressing tin ore, only 7.8% of the arsenic passes into the tin concentrate. In the case of copper and copper-zinc ores, the arsenic is concentrated in the copper concentrate to a level of around 30% of the quantity originally present in the starting ore. The copper concentrate therefore contains 0.5–1% As, and concentrates of the complex ores up to 5–8% As [3].

One example of copper ore in which a large part of the copper is bound to arsenic, as enargite or luzonite, $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$, is the Lepanto ore from the Philippines. The flotation product contains approximately 28% Cu, 32% S, and 9% As. In most ores, however, only a small proportion of the copper is bound chemically to arsenic, and the copper concentrates have a considerably lower arsenic content. Enargite-containing copper concentrates are produced in Cerro de Pasco (Peru) and Butte, Montana (USA).

In many precious metal ores, gold and silver occur together with arsenopyrite (FeAsS), löllingite (FeAs_2), and pyrites or other sulfides. Although the metals are not chemically bound to the arsenic, instead occurring as native gold and in the form of non arsenical minerals, separation by selective flotation is not satisfactory on account of a partially extensive intergrowth of the minerals. In such a case, a combined concentrate of the sulfides and arsenides – the arsenic content can vary from a few percent to more than 30% – is floated. One example is the ore from Salsigne, France, an arsenopyrite-pyrites ore containing precious metals in large quantities, some copper, and a little bismuth. The metal concentrate obtained contains ca. 23% As, 27% S, 34% Fe, 0.7% Cu, 0.6% Bi, 55 ppm Au, and 115 ppm Ag.

Arsenopyrite often occurs in pyritic copper ores, for example, on the Iberian Peninsula, in the Balkan countries, in Sweden, and in New Brunswick, Canada. The arsenopyrite can be recovered by selective flotation. Copper pyrites are removed by flotation with higher xanthates, the other sulfide minerals being held back by lime. After acidifying and heating the pulp, the pyrites and lastly, after further acidification and activation with copper sulfate, the arsenopyrite are floated. Alternatively, after flotation of the copper pyrites, the arsenopyrite may be selectively floated from the pyrites pulp after heating and activation with copper sulfate.

Table 13.2: Distribution of arsenic in the production of the concentrated raw materials (% of arsenic content in starting ore) [3].

	Complex ores	Copper and copper-zinc ores	Tin ore	Gold-bearing ore	Nickel-cobalt-bearing ore
Starting ore	100.0	100.0	100.0	100.0	100.0
Concentrates, total	15.3	41.0	17.4	35.0	1.9
Lead	7.8	—	—	—	—
Zinc	3.8	1.8	—	—	—
Copper	3.3	30.1	9.6	—	—
Pyritic	0.4	9.1	—	—	—
Tin	—	—	7.8	—	—
Gold-containing	—	—	—	35.0	—
Others	—	—	—	—	1.9
Waste products	84.7	59.0	82.6	65.0	98.1

Lead and copper concentrates rich in arsenic are produced in Mexico, South America, and South West Africa; cobalt concentrates in North Africa; and precious metal concentrates in Canada, South America, and other regions. Arsenic ores worth extracting and usable in concentrated or unconcentrated form as starting material for the production of arsenic occur in the former USSR and China.

13.5.1.2 Roasting of Arsenical Materials

Arsenic should be separated off as early as possible in the metallurgical process. Its presence in relatively large quantities complicates both pyrometallurgical and hydrometallurgical processes. Phases rich in arsenic, so-called speisses, can be formed in the reducing smelting of raw materials rich in arsenic. Because of the variety of different compositions of these speiss phases and their different solubilities in sulfide and metal melts, the speisses always lead to losses of valuable metal. Arsenic is usually unwanted in the end product metals because it adversely affects their physical properties, e.g., conductivity, and their mechanical properties, e.g., deformability [2, 4].

The removal of arsenic by refining is extremely difficult. Industrial safety regulations also dictate that arsenic be removed from metallurgical processes as early as possible.

The separation of arsenic by roasting is one possibility. The multivalency of arsenic, i.e., its ability to form more than one compound or complex with one and the same element, complicates separation. The final product should contain so little arsenic that it may be further processed as a quasi-arsenic-free material. To obtain a high arsenic removal rate and, hence, a high concentration of arsenic in as few processing steps as possible, the roasting processes must be conducted in such a way that only volatile arsenic compounds or volatile As_4 form. The formation of nonvolatile arsenates, i.e., arsenic remaining in the roasted material, must be avoided. The valuable metals remain in the roasted material as sulfite or ox-

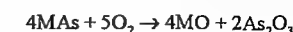
ide, depending on the starting material and the process conditions.

A relatively high oxygen partial pressure during roasting promotes the formation of metal arsenates and a poor yield of As in the flue dust. Metal arsenates are considerably more stable than the sulfates and decompose only at high temperatures.

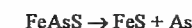
The overall course of the reaction may be written as:



At a high SO_2 partial pressure, i.e., at a low O_2 partial pressure in the roasting zone, mainly volatile arsenic oxides are formed:



As_2S_2 and As_2S_3 are volatile at low temperatures. Arsenopyrite and similar compounds decompose:

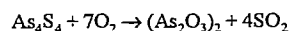


If the roasting is correctly controlled, arsenic can be separated in high yields from the most important arsenic minerals, namely, arsenopyrite, FeAsS ; löllingite, FeAs_2 ; and enargite, $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$. Nickel and cobalt arsenide minerals are much more stable and therefore more difficult to roast. Fahlores and proustite are also very stable.

Another roasting process makes use of the fact that at certain oxygen partial pressures magnetite is formed. Magnetite, in contrast to hematite, does not react with arsenic oxides to form arsenates [2]. In this process the oxygen partial pressure is adjusted by the introduction of steam and recycled roasting gases. For two roasting gases, containing 16.7% and 11.5% SO_2 , the amount of recycled gas required is calculated to be ca. 5.5% of the total quantity. The amount of air is regulated to exactly 5%. In this way an arsenic content in the roasted material of 0.01–0.05% is obtained for starting material containing 0.4% As [2].

At a low oxygen partial pressure, particularly in the case of pyrites-containing materials, the sulfur partial pressure reaches such high levels that reactions of the following type assume practical significance in the gas phase:





In the dearsenicating roasting of a raw material containing arsenopyrite or other dissociable substances, the dissociation reaction and secondary reactions are important factors. The best results are obtained by roasting at a low oxygen partial pressure. To convert all the arsenic into the trioxide, the oxidation of the dissociation products has to be completed at a relatively high oxygen partial pressure. Before cooling and purification, therefore, the roasting furnace gases are burnt under controlled conditions. If only partial desulfurization is necessary, a single-stage process is generally sufficient. For substantially complete desulfurization, however, a two-stage process may be necessary.

Roasting Plants. In principle, any standard roasting furnaces (multiple-bed and fluidized-bed furnaces, sintering apparatus and cyclones) may be used for roasting arsenical raw materials. The waste gases from the roasting reactors may also be burnt. They are then freed from dust in a hot cyclone and a hot electrostatic precipitator above the condensation temperature of As_2O_3 and subsequently cooled to 100 °C. The As_2O_3 is deposited relatively pure in a bag filter. Multiple-bed furnaces are the most suitable for dearsenicating roasting.

Multiple-Bed Furnaces. Where roasting is carried out in a multiple-bed furnace (e.g., a Wedge furnace), the atmosphere in the material bed during the first part of the roasting process should be sufficiently low in oxygen to prevent formation of arsenates. In this region most of the arsenic compounds are released from the material being roasted and are then oxidized in the atmosphere richer in oxygen over the bed of material being roasted before dust separation and cooling. Before it is discharged, the roasted material encounters the oxygen-rich fresh gas through the quantity of which the sulfur content can be adjusted to the required level. On account of the long residence time, mass diffusion is not a problem, even in relatively large particles. However, the maximum temperatures have to be limited to avoid melting and contamination. Multiple-

bed furnaces operate under reduced pressure. The flue dust content of the off-gases is relatively low.

Fluidized-Bed Furnaces. By virtue of their high roasting capacity, their low maintenance costs, and the high content of SO_2 in the off-gas, fluidized beds are being used increasingly to roast sulfidic raw materials. Raw materials rich in arsenic are roasted in fluidized beds, but to a minor extent compared with multiple-bed roasting in the production of arsenic. In contrast, the fluidized-bed roasting of pyrites poor in arsenic, with the object of separating arsenic from the ferrous raw material, has acquired considerable significance.

In fluidized-bed roasting, temperature and gas composition are easily kept constant at a level favoring separation of arsenic and subsequent complete desulfurization. The composition of the mineral, the arsenic content, and the grain size of the raw material are critical factors affecting the efficiency of arsenic separation during roasting. The roasted material is completely or partly transported with the off-gases to the gas-cleaning system, which makes gas cleaning difficult. During cooling of the gas, the arsenic trioxide can react with the metal oxides, so that the roasted material must be mechanically separated at elevated temperature. Even after this has been done, the gas still has a high flue dust content, which affects the separation of As_2O_3 and necessitates the installation of equipment for selective gas cleaning if the highest possible As_2O_3 content is to be obtained in the product.

Arsenopyrite. The roasting plant run by Boliden AB at Rönnskär and the technique it uses for roasting arsenopyrite and arsenic-containing copper pyrites concentrates are a good example of a commercial operation [5]. The multiple-bed furnace contains 9–11 hearths with a total hearth area of 230 m². The maximum roasting temperature is 500–800 °C. Most of the arsenic is actually removed in the upper hearths. Arsenic and arsenic sulfides are then allowed to burn in the roasting gas. After passing through a cyclone and a flue-dust filter, the roasted material is

cooled in a metal air cooler below the condensation temperature of As_2O_3 and purified in a hot precipitator with an exit temperature of 120–140 °C. Sulfuric acid is recovered from the gas containing 3–5% SO_2 in a fine purification plant (washing tower or wet electric precipitator). In the roasting of concentrates containing 12% As, the crude oxide accumulating in the air cooler and the hot precipitator has an As_2O_3 content of 80–95%. It is difficult to reduce the arsenic content of the roasted material below 0.5%. For roasting copper concentrates of low arsenic content, see below.

The arsenopyrite concentrates from Canadian gold mines are roasted by various methods. The end product required is a roasted material low in arsenic that is suitable for the cyanide leaching plant. For example, in the Giant Yellowknife Gold Mines, roasting is carried out in a two-stage fluidized-bed installation. The concentrate is fed directly to the first fluidized-bed reactor as a pulp for pre-roasting and is roasted to completion in a second stage. A 10–66% oxide is obtained in the electric precipitator, and the roasted material contains ca. 0.5% As for an arsenic content in the concentrate of ca. 11% [6].

In the former USSR an arsenopyrite pyrites concentrate from Darasunskii containing 9–13% As and 32–40% S is partially roasted at around 575 °C in a fluidized-bed furnace. After the roasting gas has been cleaned in a hot cyclone and a hot electric precipitator (400 °C), the oxide is separated in a condensation chamber. The roasted material contains ca. 0.5% As and 12–20% S; the oxide is 92–97% pure [7].

Arsenic-Containing Copper Concentrate. Copper smelters are the biggest producers of arsenic-containing intermediate products. The bulk accumulates in the roasting of copper concentrates containing enargite and arsenopyrite. The arsenic content of those concentrates varies within wide limits, in many cases reaching 10%. Normally the copper concentrate is roasted in multiple-bed furnaces. The process is controlled in such a way that opti-

mal conditions for removal of the arsenic prevail in the upper hearths, whereas in the lower hearths the sulfur content of the material being roasted is reduced to the level required for the subsequent smelting of low-grade matte, e.g., to 15–20%.

The processes and plants used are much like those used for the roasting of arsenopyrite (see above). Roasting is exothermic, and the maximum roasting temperature can reach 500–800 °C, depending on the composition of the batch. The yield of arsenic also depends on the composition of the batch, the type and quantity of the arsenic minerals, the roasting temperature, and other factors. For high arsenic contents or when arsenopyrite or enargite are present, the yield can be more than 80%. For lower arsenic contents the yield can be much lower because a few tenths of a percent of arsenic always remain in the roasted material.

After the hot roasting gas has been cleaned in cyclones and dust-settling chambers, relatively small quantities of a crude arsenic heavily contaminated by flue dust and volatile substances are obtained by cooling the off-gas. The As_2O_3 content of the product is generally between 10 and 50%. However, far higher contents can be obtained by using electric precipitators to remove dust from the hot gas. The dust left after cleaning of the hot gas is returned to the process.

The cleaned SO_2 -containing gas still contains traces of arsenic and other impurities that have to be removed by washing with water or a circulating washing liquid containing sulfuric acid and by final cleaning in a wet electric precipitator. The sulfur is used to produce sulfuric acid. The arsenic-containing slurries that accumulate during wet cleaning and effluent treatment are collected and neutralized to recover valuable materials.

Arsenic-Containing Pyrite Concentrates. The stocks of arsenopyrite-containing pyritic ore with < 1% As are quite large and make up a significant percentage of the raw material reserves for arsenic. Pyrites of this type are widely used as raw material for sulfur and

iron. They are also roasted to produce sulfur dioxide and iron oxides. The iron oxide must have the lowest possible arsenic content, in any case below 0.1%, and best below 0.05%. The roasting process must be conducted in such a way that as much arsenic as possible is removed. In addition, the gas must be freed completely from arsenic before it is delivered to the sulfuric acid factory or otherwise used. The products resulting from cleaning the arsenic-containing gas are being worked up to an increasing extent in the interest of protecting the environment. The most economical way is by working them up to arsenic compounds. Other constituents, such as selenium, mercury, and lead, may be obtained at the same time. In the past this way of obtaining arsenic has played a minor role. In the future, however, significant quantities of arsenic will be obtained by this method.

The traditional process for the dearsenicating roasting of pyrites is multiple-bed roasting controlled so that the arsenic is released in the low-oxygen atmosphere of the upper beds whereas the sulfur is released in the oxygen-rich atmosphere of the lower beds. The gases formed have a relatively low SO_2 content and such a high oxygen content that arsenic, sulfur, and the arsenic sulfides are completely oxidized. The As_2O_3 formed reacts further with Fe_2O_3 and oxygen to form iron arsenate. Therefore, most of the arsenic in the dust is in bound form and, in addition, because of the low total content, is an unsuitable starting material for arsenic. In recent years the multiple-bed roasting of pyrites has largely been replaced by fluidized-bed roasting.

The standard process for roasting pyrites in a fluidized bed forms Fe_2O_3 with excess air. This is unsuitable for roasting arsenic-bearing ores because the arsenic then is bound as iron arsenate in the roasted material. Two fundamentally different processes have been developed for the fluidized-bed roasting of arsenic-bearing pyrites: the two-stage BASF process and the single-stage Boliden process.

In the two-stage process developed by BASF, about one half of the sulfur present is roasted off in the first reactor at around 900 °C

at a low oxygen partial pressure. After solids and gas have been separated in a cyclone, roasting is completed in a second reactor around 800 °C in excess air. Air is added to the gas stream of the first reactor to burn the sulfides and other volatile substances still present. The gas is then cooled in a waste-heat boiler and cleaned in a hot precipitator and by washing. Some of the arsenic is present as iron arsenate in the dust precipitated, and some is washed out as As_2O_3 during wet cleaning [8, 9].

In the single-stage fluidized-bed roasting process developed by Boliden AB at Reyersholm, the pyrites are roasted in such a way that magnetite, Fe_3O_4 , is formed from the iron in the ore at a low oxygen partial pressure. In contrast to Fe_2O_3 , magnetite does not react with the As_2O_3 to form arsenate. A small amount of iron arsenate is separated with the flue dust. The gas freed from the flue dust is mixed with air to burn the dissociation products. Then it is cooled in a waste-heat boiler, freed from dust in a hot precipitator, and subjected to wet gas cleaning which separates most of the arsenic as As_2O_3 [10, 11].

In the wet cleaning of the roasting gases, the gases are washed with water or circulating sulfuric acid solutions in washing towers, Venturi scrubbers, or other apparatus and finally are cleaned in wet precipitators. Separation of the arsenic by the wash liquid is almost complete, although neutralization, utilization, or storage of the arsenic removed presents problems. Normally the process water is circulated so that a high concentration of dissolved substances builds up; a side stream is purified. For example, the arsenic may be precipitated with lime, possibly after neutralization with alkalis. Because the wash liquids are strongly acidic and contain many impurities, the consumption of chemicals is high and the product impure. Selective precipitation may be carried out. At the Reyersholm works of Boliden AB, the As_2O_3 is continuously recovered from the circulating sulfuric acid wash solution by crystallization. The product obtained serves as raw material for the production of refined As_2O_3 .

The bulk of world production of arsenic trioxide comes from the intermediate products of the roasting of arsenic-bearing ores, above all copper ores, lead ores, and arsenopyrite ores. Therefore the level of arsenic production is limited by the amount of metals production. The raw material base will likely increase through the exploitation of low-grade by-products.

13.5.1.3 Production of Refined As_2O_3

Preliminary Concentration. The starting material for the industrial production of refined As_2O_3 is the arsenic-rich dust or slurry that accumulates as an intermediate product in the roasting and smelting of arsenic-bearing ores and concentrates. The bulk of this arsenic raw material comes from copper smelters, although some also comes from lead, cobalt, and other smelters. Occasionally, in the former USSR and possibly China, arsenic-rich ore is roasted with the primary object of recovering arsenic. All these raw materials of various origins and arsenic contents have in common that they are obtained as products of gas cleaning and also contain other condensation products and flue dusts. Arsenic is mainly present as As_2O_3 , although some may also be bound as arsenite or arsenate. The arsenic content can vary enormously, depending on the ore used and the way in which roasting and gas cleaning are carried out. The gas-cleaning products often contain other valuable constituents and, because of this, must be worked up even if the arsenic content is very low. In such cases the materials are circulated until the arsenic content exceeds 10%. Low-grade gas-cleaning products of low As_2O_3 content from copper and lead roasting plants contain flue dust from the furnace charge as their principal impurity, whereas the high-grade products mainly contain volatile impurities, such as lead, antimony, bismuth, and selenium. Most of the impurities are present as oxide or sulfate.

Low-grade starting materials are treated in a multistage process. In the first stage the material is roasted to produce $\geq 80\%$ As_2O_3 . This

is sublimed and separated from the roasting gases. The bulk of the impurities remains in the roasted material, which is returned to the original process or treated separately to recover valuable secondary products. To increase the yield of arsenic and to facilitate the movement of material through the roasting furnace, sulfides or charcoal are added as reducing agents to the furnace charge. The reducing atmosphere thus established in the material decomposes the metal arsenates and no more arsenate is formed. For example, dust from the gas-cleaning process is mixed with a few percent of iron pyrites concentrate, and the resulting mixture heated at 300–500 °C in oil-fired multiple-bed furnaces. The arsenic-containing gas is cooled in a long brick pipe, passes through a flue-dust chamber, and then through several chambers in which the temperature falls from 220 °C to below 100 °C to separate the arsenic. Finally the gas is cleaned in bag filters. In this system the flue dust and gaseous impurities of low vapor pressure are separated preferably in the first part of the system, so that the gas-cleaning process is fractionated. In a critical temperature range above 200 °C, a relatively small quantity of impure, amorphous glassy arsenic trioxide accumulates. However, most of the arsenic trioxide obtained is crystalline. A product containing the high vapor pressure impurities is separated in the bag filter.

Some of the crude arsenic from the separating chambers containing more than 95% As_2O_3 is sold, but most of it is refined further. The less pure products are returned to the process.

Refining. High-purity crude oxide, obtained either directly or via concentration processes, can be dry refined by sublimation or wet refined by dissolution and crystallization.

The widely used sublimation process is carried out by heating the crude arsenic in a reverberatory furnace. The gases are passed through a dust-settling chamber to a ca. 70-m-long system of, e.g., 39 brick arsenic separation chambers called kitchens. The kitchens are followed by a bag filter. The temperature

in the dust-settling chamber is kept at ca. 295 °C, which is considerably above the condensation temperature of arsenic trioxide. The temperature of the bag filter is kept at 90–100 °C. A black, amorphous arsenic trioxide containing ca. 95% As_2O_3 accumulates in the first kitchens. In the following kitchens, in the temperature range from 180 to 120 °C, most of the arsenic trioxide accumulates in a crystalline form analyzing more than 99%. The product separated in the last kitchens below 120 °C and in the bag filters assays ca. 90% As_2O_3 . The low-purity products are returned to the process or, if they assay more than 95% As_2O_3 , are sold as crude arsenic. The high-purity products from the middle kitchens are marketed as white arsenic.

Several versions of the dry refining process, e.g., with repeated sublimation, have been described in the literature. The Rönnskär works have developed a process for the production of nondusting white arsenic by shock cooling of hot-cleaned sublimation gas.

The wet refining of crude oxide was introduced at the Rönnskär works back in the 1930s and is now the only refining process practiced here. The process is based on the large temperature coefficient of the solubility of As_2O_3 in water (12.1 g/L at 0 °C, 18.1 g/L at 20 °C, 81.8 g/L at 98.5 °C), on the low solubility of the impurities, and on the purification accompanying crystallization of the As_2O_3 .

The crude oxide, assaying from 80 to 95% As_2O_3 , is brought in a closed system to the refining plant and pressure leached in steam-heated autoclaves with water or circulating solution. The As_2O_3 dissolves, whereas the impurities, such as oxides, sulfides, sulfates, and arsenates of lead, bismuth, antimony, iron, and other metals, as well as silica, selenium, and other substances, form a slightly soluble sludge, which is separated from the hot leaching solution. The solution is vacuum cooled, and the crystallization is controlled to give a relatively coarse product, which is separated by centrifuging from the solution, washed, dried, and packaged in a closed system. The mother liquor is recycled. The process is fully continuous and also satisfies stringent indus-

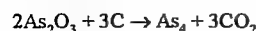
trial hygiene requirements. The wet-refined arsenic contains more than 99% As_2O_3 and is marketed as white arsenic, either in metal casks or in lined wooden casks.

13.5.2 Production of the Metal

Metallic arsenic is produced on a fairly wide scale as commercial arsenic metal, primarily as an additive for alloys, and to a lesser extent as high-purity arsenic for electronic applications.

Commercial Arsenic Metal. The starting material for the production of a metal of commercial quality is usually white arsenic. However, the metal can also be produced from arsenopyrite or löllingite.

In the processing of As_2O_3 the oxide is normally reduced with carbon:



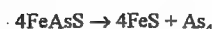
The reaction is endothermic and is carried out at 500–800 °C. The elemental arsenic sublimates and is condensed out of the reaction gas by cooling.

There are several versions of the carbon reduction process. In one version a mixture of As_2O_3 with 25% charcoal is placed in a horizontal steel retort jacketed with firebrick and heated to 650–700 °C in a gas-fired furnace. The reaction gas is collected in water-cooled condensers, in which the metal separates as crystals. After about 10 h, the heating is stopped, and, after the furnace has cooled, the metal can be removed from the condensers.

Similar processes are thought to have been used by several producers. For example, at the Rönnskär works of Boliden AB, steel retorts are provided with demountable air-cooled condensers. After the cold retorts have been charged, they are closed and heated to 700–800 °C in an electric furnace. The metal is separated in the condenser, while the off-gases are cleaned in a scrubber system. Most of the metal is coarsely crystalline. After size reduction and grading, the arsenic is packaged in metal casks. In the process used at the Reichenstein works in Silesia, As_2O_3 was vaporized by indirect heating in a gas-heated retort

furnace, and the vapor was passed through a 3-m-tall incandescent coke layer into a tower reactor in which it was reduced to gaseous arsenic. The metal was separated in large condensers arranged in series.

Carbon monoxide [12] or ammonia [13] may also be used as reducing agents. Metallic arsenic may be obtained from arsenopyrite or löllingite by thermal dissociation:



V. G. RCHILADZE [14] described the theory of this process in detail and suggested how it may be carried out in practice. Arsenopyrite is placed in steel retorts lined with diabase or basalt and heated electrically in two stages to 700–900 °C. This causes the arsenic and a small quantity of sulfur compounds to volatilize. The metal vapor is condensed at 450–500 °C in an electrically heated steel condenser. The metal is scraped off the condenser walls and cooled in a closed system. The volatile sulfur compounds are separated from the off-gas at a lower temperature. The purity of the metal depends on the ore, specifically on the content of volatile impurities that condense under the same conditions as the arsenic. Some sulfur content is always present. In an experiment, metal containing more than 99% As was obtained from arsenopyrite assaying from 25 to 45% As. The principal impurities were sulfur and bismuth.

Practical experience in the production of metallic arsenic by reduction with carbon has shown that there are many difficulties. The danger to personnel and the risk of explosion are the two most important. In addition, As vapor is highly corrosive, so that the useful life of the plant is shortened significantly [15]. To overcome these problems, attempts are being made to produce metallic arsenic in other ways. Crystallized As can be obtained from AsCl_3 , As_2S_3 , or As_2O_3 by gas-phase reduction with hydrogen. The hydrogen required for reduction is produced in situ by the thermal dissociation of ammonia. The reduction is highly exothermic. This process is said to give an arsenic yield of 93–98%. The off-gas contains

70% N_2 and 30% hydrogen. An advantage lies in a certain degree of refining that takes place. Table 13.3 shows one example of how impurities present in As_2O_3 affect the purity of the metallic arsenic. Figure 13.1 shows a schematic diagram for one such plant.

Table 13.3: Refining effect in the reduction of As_2O_3 with H_2 .

	As_2O_3 , ppm	As, ppm
Ag	<1	<0.1
Al	7	1
Bi	2	2
Ca	9	3
Cd	<1	<1
Co	<1	<1
Cu	5	2
Mg	3	<1
Mn	<1	<1
Na	20	<10
Ni	<1	0.3
Pb	10	0.5
Sb	1000	0.2
Zn	3	3
Cr	<1	<1
Fe	20	8
Si	50	10
Sn	<1	<0.3
Te	<30	<10

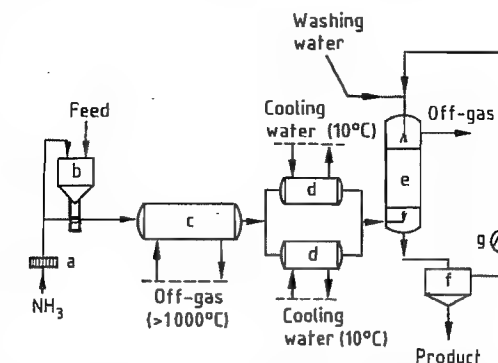


Figure 13.1: Plant for producing crystalline arsenic metal: a) Roots blower; b) Reservoir; c) Reactor; d) Condensers in parallel; e) Washing tower; f) Decanter; g) Pump.

Another way of obtaining metallic arsenic is to sublime a Pb–As–Sb alloy to give 99% pure arsenic metal. Flue dust containing antimony and arsenic and a lead-containing residue from the electrolytic refining of Pb are reduced with carbon to a lead alloy containing 7–12% As and 18–30% Sb. A 90% As con-

taining 10% Sb and 0.05% Cd is produced in a first vacuum distillation stage carried out at 480–590 °C (Figure 13.2).

A 99% As suitable for the commercial market is obtained in a second vacuum distillation stage carried out after removal of the cadmium from the residue [16].

Commercial arsenic produced from As_2O_3 contains > 99% As and as its main impurities antimony and oxygen. This quality is used primarily for the production of alloys.

High-Purity Arsenic. Arsenic is produced in various high-purity grades for special applications. A limited refining effect can be obtained by resubliming commercial metal in a stream of hydrogen. In general, however, various purification stages are combined in the production of high-purity metal.

Commercial arsenic is sublimed, reacted with oxygen to produce As_2O_3 which is recrystallized from aqueous hydrochloric acid, sublimed in a stream of hydrogen, and then reduced to the metal with hydrogen at 800–850 °C. The arsenic obtained has a purity > 99.999% [17]. The process most often reported in the literature uses white arsenic as its starting material. This is reacted with hydrochloric acid to form arsenic trichloride [18]. The arsenic trichloride is purified by fractional distillation, possibly in combination with chemical methods, and is reduced by reaction with hydrogen in a tube heated to 500–900 °C. The metal vapor is condensed at 300–500 °C to crystalline form. After sublimation, the metal is packaged in glass ampules. An arsenic content of > 99.999(9)% can be obtained by this method. The number in parenthesis indicates the limits of analytical accuracy.

Table 13.4: Content of impurities (% by weight) in two samples of pure arsenic (Content of Ni, Bi, Pb, Cr, and Mn in all samples, < $5 \times 10^{-6}\%$; Sb, In, Sn, and Cd, < $5 \times 10^{-3}\%$).

	Sample no.	Cu $\times 10^6$	Al $\times 10^5$	Fe $\times 10^5$	Si $\times 10^5$	Mg $\times 10^5$	S $\times 10^5$
After reduction	1	1	1	0.5	10	4	7
	2	1	0.5	1	5	2	20
After distillation in hydrogen	1	1	0.5	1	1	1	5
	2	1	2	1	2	2	2
After vacuum distillation	1	1	0.5	1	2	1	2
	2	1	1	1	1	1	2

Figure 13.3 shows the distribution of arsenic in the production of semiconductor-purity arsenic. The yield is 62%. Table 13.4 shows the impurities present in the high-purity arsenic after the individual process steps [19].

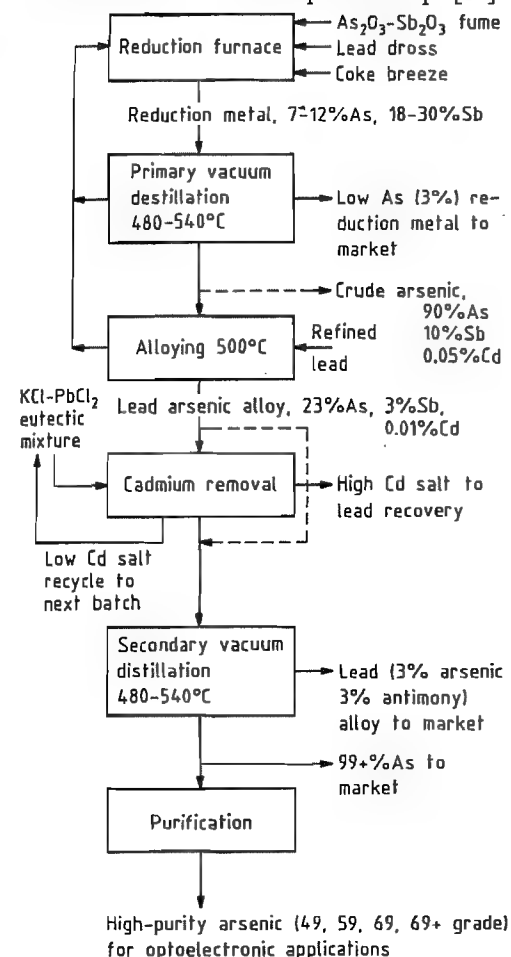


Figure 13.2: Flow sheet of the Cominco recovery process.

Table 13.5: Circulation of arsenic in lead and copper smelters (% of total arsenic in circulation).

	Lead processing						Copper processing		
	1*	2	3	4	5	6	7	8	9
Arsenic in circulation	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Dusts	33.0	24.5	32.8	19.4	12.3	68.6	77.2	34.7	—
Slags	0.3	0.3	0.9	2.0	3.4	2.9	21.4	65.3	100.0
Dross	65.3	73.8	49.1	41.0	69.1	15.4	—	—	—
Unconditioned matte	0.7	—	8.2	—	15.2	—	—	—	—
Melt	—	—	—	31.8	—	8.2	—	—	—
Others	0.7	1.4	9.0	5.8	—	4.9	1.4	—	—
Arsenic in circulation in %, based on the total used	52.1	5.8	14.0	11.1	3.3	2.9	3.6	4.3	2.9

*The numbers 1 to 9 stand for different lead resp. copper producers.

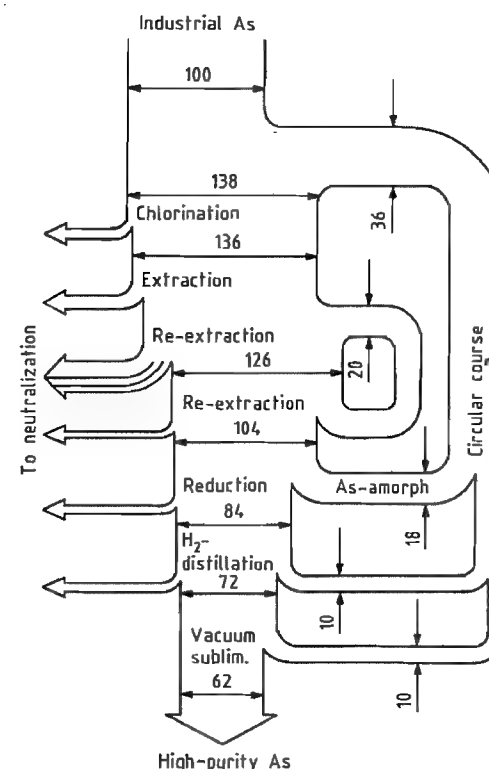
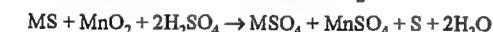


Figure 13.3: Material flow in the production of semiconductor-purity arsenic by the chloride method.

significant drop in demand. On the other hand, increasing quantities of arsenic-containing by-products are accumulating as the production of heavy metals increases. These products build up in the material circuits of the individual factories [20]. Ultimately, arsenic-containing materials have to be removed from those circuits. The processes involved are very cost intensive. In addition, if the demand for As is inadequate, special measures must be taken to dispose or store those materials [21]. In lead smelters, for example, considerable amounts of As forerun come from circulating materials.

Table 13.5 shows the distribution in flue dusts, slags, dross, and matte in copper and lead smelters. Most of the arsenic in lead processing circulates in the form of flue dusts and copper dross. In copper processing the main arsenic carriers are flue dust and slags [3].

In recent years various methods of removing the As have been examined. For example, a lead-copper matte containing 25.7% Cu, 18.2% Ni, 1.65% Co, 27.2% Pb, and 4.14% As is leached with concentrated H_2SO_4 at 85–100 °C in the presence of MnO_2 :



(M = Cu, Ni, Co, and Pb)

The metals Ni, Co, Fe, and As dissolve, leaving a residue of elemental sulfur and $PbSO_4$. The residue is separated. As is precipitated as $FeAsO_4$ by addition of NaOH or $Ca(OH)_2$ at pH 4. The $FeAsO_4$ takes up 88–92% of the arsenic. It consists of 24% As, 22% Fe, and 3–5% Cu and is in a suitable form for safe disposal [22, 23]. As shown in

13.6 Treatment of Arsenic-Containing By-products

Arsenic and products containing arsenic are under an increasing barrage of criticism, because of their toxicity. This has produced a

Figure 13.4, the remaining solution is processed further to remove Co and Cu and recover MnO_2 .

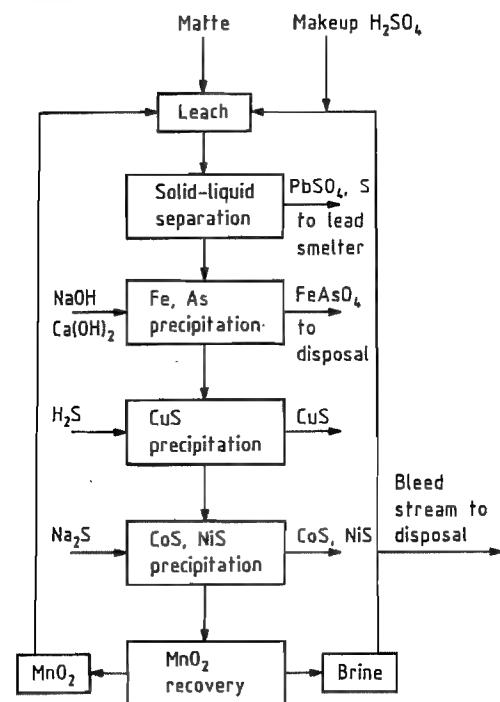


Figure 13.4: Flow diagram for recovery of cobalt, nickel, and copper from mattes [20].

Arsenic-containing lead flue dusts can be leached with a 20% H_2SO_4 at 90 °C. More than 90% of the As, Zn, and Cd pass into solution. The residue rich in lead is returned to the lead production process. After removal of the indium from the solution by solvent extraction, the arsenic is precipitated with $\text{Fe}_2(\text{SO}_4)_3$ and CaCO_3 as an iron-containing arsenic residue suitable for storage in containers or for

further treatment. Table 13.6 shows the typical composition of three different lead smelter flue dusts. Figure 13.5 shows a flowsheet [24]. Arsenic also can be precipitated with calcined zinc concentrates [23], H_2 , Na_2S , or even NaHS . Either As_2S_3 or As_2S_5 is obtained [25].

Another method of removing As from copper smelter flue dusts is based on an oxide leach at $p_{\text{O}_2} = 9$ bar in copper sulfate electrolyte. In the case of a material containing 13.9% Cu, 2.05% Zn, 5.6% Fe, and 9.51% As, about 87% of the As stays in the iron-containing residue. All the valuable metals pass into solution.

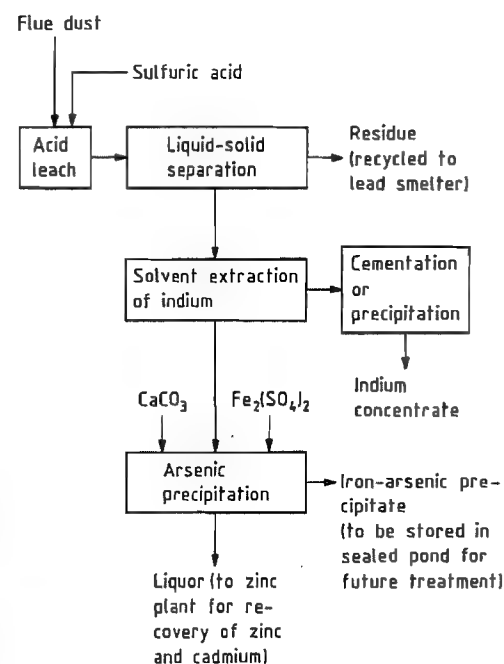


Figure 13.5: Flow sheet for treatment of lead smelter copper dress flue dust.

Table 13.6: Assays of lead smelter flue dust samples.

Sample	Description	Assay, %								
		As	Pb	Zn	Cd	Sb	In	Cu	Fe	SO_4^{2-}
1	Composite sample	10.0	41.0	10.3	0.79	3.5	0.26	0.10	0.28	7.0
2	Dry sample	10.0	51.0	16.2	0.22	1.4	0.36	0.16	0.03	6.9
3	High-zinc sample	7.0	45.0	21.0	0.20	2.4	0.55	0.21	0.40	9.8

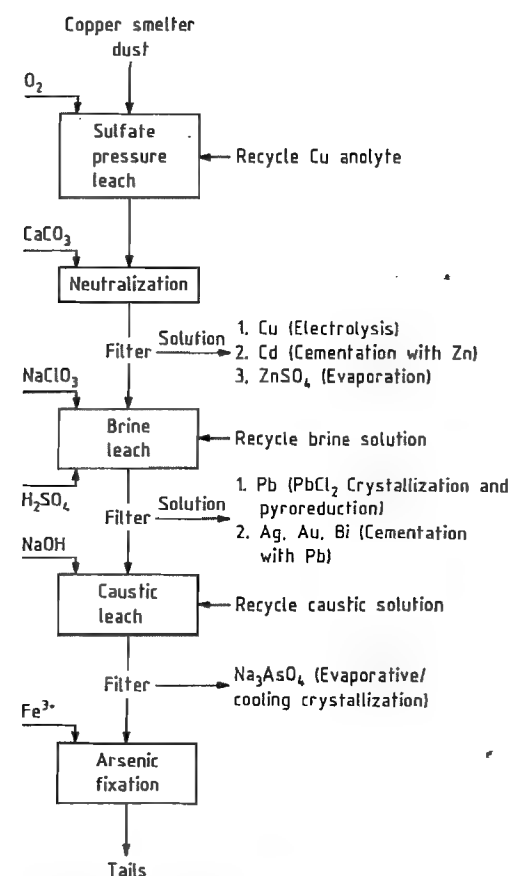


Figure 13.6: Process for recovering metal values from materials containing arsenic.

Figure 13.6 shows a multistage process in which Cu, Cd, and Zn are separated off in solution after a neutralization step. Arsenic is precipitated together with lead and the precious metals. Lead and the precious metals are dissolved in a further chloride-sulfate leaching step. During a subsequent alkaline leaching step, the As is dissolved as Na_3AsO_4 and then crystallized out. By adding iron(III) sulfates, the soluble arsenic constituents are precipitated. An iron arsenide residue suitable for disposal is obtained. Tests to determine the solubility of arsenic from such a residue in acidic solution revealed a content of < 0.4 ppm As after 5 d [26].

Wet metallurgical processes, in which the As is separated beforehand from the concen-

trates, are now fully operational. A silver-rich copper concentrate containing 17% Cu, 7000 g/t Ag, 19 g/t Au, 8% Sb, and 3% As is treated as illustrated in Figure 13.7. At the heart of the process are two autoclaves for the removal of Sb and As. The arsenic is converted by treatment with CaO into insoluble $\text{Ca}_3(\text{AsO}_4)_2$. The production of calcium arsenate requires O_2 pressures of 1.5 MPa (15 bar) at temperatures of 190 °C. The calcium arsenate crystals are centrifuged off and dehydrated in a filter press to produce 600 t/a of calcium arsenates [27].

Arsenic is said to be removed from gold-containing flotation concentrates by a vacuum-thermal method [28].

Sodium sulfate melts are said to remove 84% of the As from blast furnace flue dusts [20].

Another proposal for avoiding nondisposable products: The atmosphere prevailing during the roasting of tin ore concentrates in a multiple-bed furnace is regulated so that As volatilizes as As_4 . The oxygen and sulfur partial pressures can be adjusted so that the As_4 is converted by two additional burners, for example in a tube reactor, at 600–900 °C into disposable, water-insoluble As_4S_6 , which is recovered in the sump of a washer. The product is suitable for disposal or, if desired, may be worked up to marketable products [29].

13.7 Compounds

The most important use of arsenic compounds is the production of arsenic-containing pesticides, although even here consumption is very much on the decline because of environmental pollution and toxicity [30–33].

13.7.1 Arsenic Trioxide

As_2O_3 is also known as white arsenic. It occurs in two crystalline and one amorphous modification. The octahedral (or cubic) modification, arsenolite, ρ 3.86 g/cm³, is stable at room temperature. It is formed on condensation of As_4O_6 vapor, As_4O_6 molecules are the lattice units. At temperatures above 221 °C, it changes into a monoclinic modification, claudetite, ρ 4.15 g/cm³.

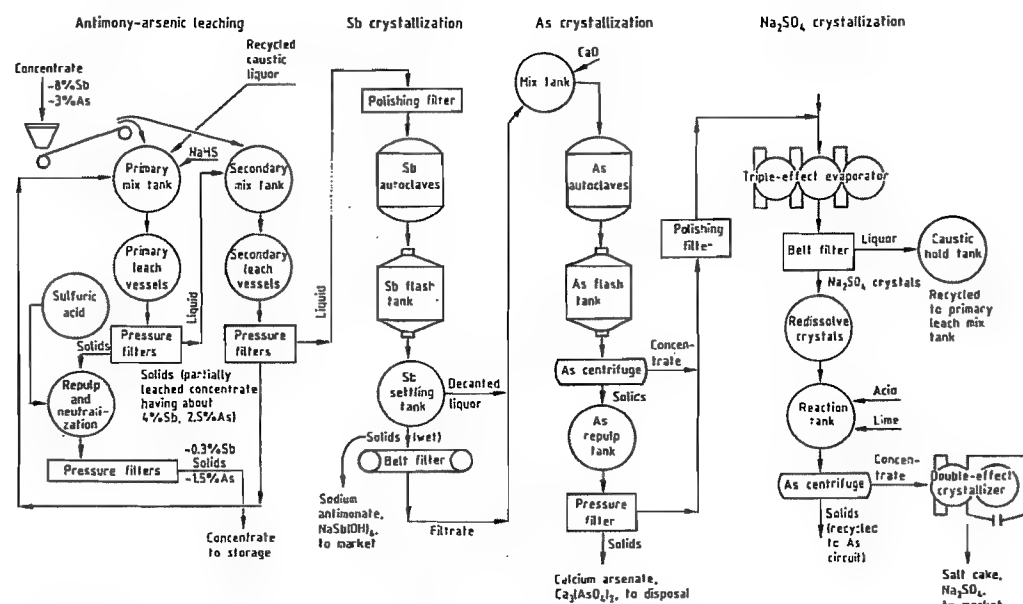


Figure 13.7: Simplified schematic flow sheet of leach plant at Equity Silver Mines Ltd.

This modification is directly formed when condensation is carried out at temperatures above 221 °C. Condensation above 250 °C results generally in the formation of the amorphous, glassy phase, ρ 3.70 g/cm³, which devitrifies into the octahedral modification at room temperature.

In an open vessel, arsenic trioxide sublimes without melting above 135 °C. The monoclinic form melts at 312.3 °C under its own vapor pressure. Up to about 800 °C the vapor density corresponds to the formula As_4O_6 ; at 1800 °C, dissociation into As_2O_3 molecules is complete. The As_4O_6 molecules were also detected in nitrobenzene solutions.

Arsenic trioxide is moderately soluble in water. The glassy-amorphous As_2O_3 dissolves much more easily than the crystalline form; its solubility is 12 g/L at 2 °C and 114.6 g/L at 100 °C [34]. The solution has a sweetish taste with an unpleasant metallic tang. As little as 0.1 g can be fatal, if As_2O_3 enters the stomach.

13.7.2 Arsenous Acid

Arsenous acid cannot be obtained from aqueous solutions of As_2O_3 ; instead, As_2O_3 is

reprecipitated. However, in aqueous solution it exists in equilibrium with its dissociation products. It is still not clear what formula should be assigned to dissolved arsenous acid. In addition to the formulation as orthoacid, H_3AsO_3 or $\text{As}(\text{OH})_3$, which is used here, the dissolved acid may also be formulated as metaacid, HAsO_2 or $\text{AsO}(\text{OH})$, or as hexahydroxoacid, $\text{H}_3[\text{As}(\text{OH})_6]$. Arsenous acid is amphoteric, dissociating in two ways:



The dissociation constants are 6×10^{-10} and 1×10^{-14} , respectively. Accordingly, arsenous acid is a very weak acid, approximately equal in strength to boric acid, but it is a much weaker base. The As^{3+} ions occur in significant quantities only in very strongly acidic solutions.

Arsenates(III). The salts of arsenous acid are called arsenates(III). Formerly they were called arsenites. Some salts exist in the forms MH_2AsO_3 , M_2HAsO_3 , and M_3AsO_3 , although most salts of arsenous acid are derived from

the metaacid, HAsO_2 , i.e., have the formula MASO_2 .

The alkali-metal arsenates(III) dissolve easily in water, whereas the alkaline-earth arsenates(III) are slightly soluble to insoluble. The compounds of arsenous acid with heavy metals are insoluble in water. Arsenous acid can be retained in considerable quantities by slimy metal oxide hydrates, such as iron oxide hydrate by adsorption.

The arsenates(III) are decomposed by strong acids because they are salts of a very weak acid.

Sodium arsenate(III), NaAsO_2 . does not exist in crystallized form. Solutions of the salt are obtained by dissolving arsenic trioxide in sodium hydroxide. For manufacture, arsenic trioxide is mixed with caustic soda. After the addition of a little water, a vigorous reaction begins, spreading quickly through the mixture. Soda may also be mixed with the oxide and a little water, and the resulting mixture dried at elevated temperature in a furnace. In both cases, a water-soluble product is obtained after grinding. It is used in the manufacture of insecticides, herbicides, etc.

Other arsenates(III): Many complex metal arsenates(III) are known. They include *Scheele's green*, formerly used as an artist's color. It is a mixture of copper arsenates(III) to which formulas such as $\text{Cu}_3(\text{AsO}_3)_2$, CuHAsO_3 , and $\text{Cu}(\text{AsO}_2)_2$ have been assigned. The double salt of copper arsenate(III) and copper acetate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$, is *Schweinfurth green*, another artist's color. This use has declined enormously because of the poisonousness. Calcium and copper arsenates(III) were formerly used as "*copper-arsenic liquor*", to control pests in viniculture.

13.7.3 Arsenic Pentoxide

Arsenic pentoxide, As_2O_5 , is a white glassy mass (ρ 4.32 g/cm³), which deliquesces in air to form arsenic acid. On heating, arsenic pentoxide begins to decompose near its melting point, ca. 300 °C. The vapor consists of arsenic trioxide and oxygen. The pentoxide can

be prepared by reaction of arsenic trioxide with oxygen under pressure or by dehydration of crystalline arsenic acid at temperatures above 200 °C [35]. The crystal structure was unknown until recently. The monocrystals were grown under oxygen excess pressure: space group $\text{P}2_12_12_1$ [36, 37].

13.7.4 Arsenic Acid

Arsenic acid, H_3AsO_4 , is known in the solid state only as the hemihydrate $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$ in the form of rhombic, deliquescent crystals. Solutions in water behave as a tribasic acid with the dissociation constants $K_1 = 5.6 \times 10^{-3}$, $K_2 = 1.7 \times 10^{-7}$, and $K_3 = 3 \times 10^{-12}$. Arsenic acid loses water when heated to 120 °C with the formation of pyroarsenic acid, $\text{H}_4\text{As}_2\text{O}_7$. At higher temperatures, more water is lost and metaarsenic acid, HAsO_3 , forms [35]. If the protons of the acids are completely or partly replaced by metals, the arsenates(V), which generally correspond to the phosphates, are formed. In acidic solution, arsenic acid and its salts are strong oxidizing agents.

Production. Arsenic acid is produced solely by the oxidation of As_2O_3 . Various processes for its production based mostly on oxidation with nitric acid, which gives a high yield, are described in the patent literature. Originally the apparatus used for those processes were usually made of stoneware but they are now made of alloys resistant to nitric acid.

The plant usually consists of so-called developers and a regenerator for nitric acid. The developers are ca. 4-m³ vessels equipped with a high-speed stirrer, a steam coil, and a mechanical feeder for oxide. About 2000 L of 38% HNO_3 is introduced initially, and the oxide is run in with strong heating until the nitric acid has been consumed. The oxides of nitrogen formed pass from the developer into the regenerator, where they are worked up to nitric acid in the presence of air and water. Up to 90% of the NO and NO_2 formed are converted back into nitric acid. One developer can process 2000 kg of As_2O_3 into arsenic acid in 24 h.

Oxidation with sodium or calcium chlorate also enables a relatively large quantity of oxide to be oxidized in a short time. The oxide is suspended in water and a little arsenic acid is added to the resulting suspension. An aqueous solution of the chlorate is run in at boiling temperature. The reaction takes place smoothly while chlorate is uniformly run in. The input of chlorine must be reduced towards the end of the reaction because otherwise chlorine readily escapes. The arsenic acid obtained by the chlorate process always contains chloride, which causes problems in the production of lead arsenate.

Arsenic acid is used as a defoliant and as a starting material for important inorganic and organic arsenic compounds.

Arsenates(V). Arsenic acid gives three series of salts. They correspond generally to the phosphates in their compositions and solubilities. Many of them are also isomorphous with the phosphates, e.g., ammonium magnesium arsenate(V), $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, which changes on calcination into magnesium pyroarsenate(V), $\text{Mg}_2\text{As}_2\text{O}_7$, a form suitable for the quantitative determination of arsenic acid. Unlike silver phosphate, which is yellow, the silver salt Ag_3AsO_4 is brown.

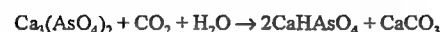
Of the numerous salts of arsenic acid, the salts of potassium, sodium, calcium, and lead are important commercially. Even today they are used on a wide scale in pest control, although modern synthetic organic compositions have reduced the use of arsenates. In some countries, the use of arsenic compounds in plant protection agents has been banned. The same applies to metal arsenates(V) as active constituents of arsenic-containing wood preservatives [38, 49].

Monopotassium arsenate(V), KH_2AsO_4 , $\text{mp } 288^\circ\text{C}$, $\rho \text{ 2.867 g/cm}^3$, was used in the manufacture of insecticides and in the preservation of skins. It is prepared by calcining a mixture of equal parts of arsenic oxide and potassium nitrate in cast-iron cylinders, leaching the melt with water, and concentrating the solution with arsenic acid. It forms white crystal crusts.

Trisodium arsenate(V), $\rho \text{ 1.759 g/cm}^3$, $\text{mp } 86.3^\circ\text{C}$, is obtained most easily by neutralizing arsenic acid with sodium carbonate or sodium hydroxide. Concentration by evaporation gives a marketable product having the formula $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$.

Disodium arsenate(V), Na_2HASO_4 , $\rho \text{ 1.72 g/cm}^3$, is obtained by roasting a mixture of arsenic oxide with sodium carbonate and sodium nitrate in the presence of air. In addition, this compound can be easily obtained by calcining sodium arsenate(III) in the presence of air. Sodium arsenate(V) is used in the production of other arsenates, such as calcium and lead arsenates.

Calcium arsenates(V). There are three known calcium salts of arsenic acid, $\text{Ca}(\text{H}_2\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHASO}_4 \cdot \text{H}_2\text{O}$, and $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$. In addition, there are basic salts, for example, $\text{Ca}_5\text{OH}(\text{AsO}_4)_3$, which corresponds to apatite. Commercial preparations are based on the neutral salt. However, different manufacturers use different methods and do not always guarantee the production of a strictly neutral salt. Because of the risk of damage to plants that acid arsenic salts involve, a basic character is given to the commercial product during its production by using excess lime. Elevated temperature, abundant moisture, and atmospheric carbon dioxide cause calcium arsenate to convert into the plant-damaging acid arsenate:



The reason the acid salt is harmful is its greater solubility in water, 0.31% As_2O_5 vs. 0.013% for the neutral salt. The neutral salt begins to turn acid only after the excess lime added has been converted completely into carbonate. For the solubility in the presence of atmospheric carbon dioxide, see [33].

Calcium arsenate(V) is generally prepared by reacting milk of lime with arsenic acid. Maintaining a certain temperature and an experimentally determined feed rate and stirring speed, the arsenic acid can be run as a fine distribution into the milk of lime. The precipitate obtained is filtered, washed, and dried.

Calcium arsenate(V) is also obtained by heating calcium arsenate(III) in a stream of dry air.

Lead arsenate(V), PbHASO_4 , is a white water-insoluble powder of density $\rho \text{ 5.79 g/cm}^3$. It was marketed as a plant protection agent in the form of powders and pastes. It is produced mainly from lead acetate, lead nitrate, and lead oxide and disodium arsenate. The direct reaction of arsenic acid with litharge in the presence of nitric acid gives a dilead arsenate. Commercial lead arsenates contain mostly PbHASO_4 along with varying amounts of $\text{Pb}_3(\text{AsO}_4)_2$. Accordingly, their lead content is higher and their As_2O_3 content lower than the levels calculated for PbHASO_4 .

Arsenic-containing plant protection agents have been banned in Europe. However, they are still used in East Asia [38, 49].

13.7.5 Arsenic Sulfides

Table 13.7 shows some physical data of the arsenic sulfides [34, 39].

Table 13.7: Physical data of arsenic sulfides.

	Color	mp, °C	bp, °C
Arsenic disulfide (re-algar)	red	307	565
Arsenic(III) sulfide (orpiment)	yellow	320	707
Arsenic(V) sulfide	yellow	> 95 decomp.	—

Arsenic disulfide, As_4S_4 (realgar, red arsenic glass, red glass, ruby arsenic, arsenic blend), occurs in ruby-red crystals or as an amorphous reddish mass. Its commercial value is determined less by the chemical composition than by its purity and fineness. Industrially produced red arsenic glass varies in its composition. Whereas the red glasses previously contained 70% As and 30% S, substantially corresponding to the formula AsS , they now contain around 61–64% As and 39–36% S. The red glass is marketed in finely divided form.

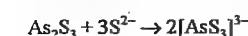
Red glass has long been produced on a large scale from arsenic ores and sulfur ores or from arsenopyrite containing iron pyrites. Another industrial process based on production

from arsenous acid and sulfur has recently been perfected. Prolonged development problems were presented by discolored products that had to be converted into an attractive, marketable red glass. The red glass is produced in two separate steps. A red glass that does not yet have the desired composition and that needs refining in appearance is obtained in the first step by melting and sublimation. The intermediate product is therefore refined and is given the required color.

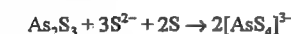
Production by melting a mixture of elemental arsenic and sulfur gives a red glass particularly fine in appearance but too expensive on account of the high price of the elemental arsenic. The processing of arsenopyrite and sulfur, although possible, is not usual.

Most red glass is used in tanneries as a depilatory in the manufacture of fine leather.

Arsenic(III) sulfide, As_4S_6 , occurs as a yellow mineral known as orpiment. It can be produced by precipitation of compounds of trivalent arsenic with hydrogen sulfide. The colloidal solution of the arsenic trisulfide can be flocculated by hydrochloric acid, in which it is insoluble. However, it dissolves readily in basic reagents, above all in alkali-metal sulfide solutions, including ammonium sulfide, to form thioarsenites:



If yellow ammonium hydrogen sulfide is allowed to act on arsenic trisulfide, the dissolved sulfur promotes oxidation to thioarsenate:



Arsenic trisulfide is a lemon-yellow compound, which begins to sublime before melting, melts at 310°C to form a red liquid, and boils at 707°C without decomposing. It is used as an artist's color, marketed in pure form as king's yellow. The impure product obtained by fusing arsenic trioxide with sulfur is marketed as orpiment. Orpiment always contains unchanged arsenic trioxide and, unlike the pure sulfide, is poisonous.

Orpiment was once used for cosmetic purposes. It is now used in the semiconductor in-

dustry, for the production of IR-permeable windows, and as a pigment.

Arsenic(V) sulfide, As_4S_{10} , is produced by fusing stoichiometric quantities of As and S powder or by precipitation from highly acidic arsenate(V) solution with H_2S . At relatively high temperatures As_4S_{10} decomposes into arsenic(III) sulfide and sulfur.

13.7.6 Arsenic Halides

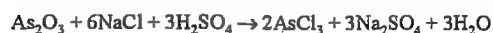
The known arsenic halides are listed in Table 13.8 [34, 39, 40].

Table 13.8: Physical data of arsenic halides.

	Form	mp, °C	bp, °C
Arsenic(V) fluoride	colorless gas	-88.7	-58.2
Arsenic(V) chloride		-50 (decomp.)	—
Arsenic(V) oxychloride	colorless liquid	-78	—
Arsenic(III) fluoride	colorless liquid	-8.5	60.4
Arsenic(III) chloride	colorless liquid	-13	130.2
Arsenic(III) bromide	yellow liquid	31	221
Arsenic(III) iodide	red solid	140.7	ca. 400

All arsenic halides can be produced by direct combination of the components. They can also be obtained by halogenation of the oxides or sulfides. The bonds are hydrolyzed by water. Only arsenic(III) chloride is commercially significant.

Arsenic trichloride, AsCl_3 , is a colorless oily liquid that fumes in air, ρ 2.17 g/cm³. By virtue of its low boiling point, AsCl_3 is easy to separate from SbCl_3 and the chlorides of other metals. $\text{As}(\text{OH})_3$ forms during hydrolysis. The direct synthesis of AsCl_3 is uneconomical. An old commercial production method is the Glauber process using arsenic trioxide:



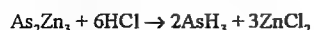
However, AsCl_3 is easier to produce by reacting As_2O_3 with gaseous hydrogen chloride at 180–200 °C.

Arsenic(III) chloride is a starting material for numerous organoarsenic compounds and for the preparation of chlorine derivatives of the arsines. It is used as a dopant in the manufacture of semiconductors and in the production of high-purity arsenic metal [41].

13.7.7 Arsenic Hydride and Arsenides

Arsenic hydride, AsH_3 , arsine, bp -55 °C, mp -116.3 °C, is the only known hydrogen compound of arsenic; it is a colorless gas with an unpleasant, garlic-like odor. It is extremely toxic: in many cases the inhalation of small amounts has caused death. Arsine does not ignite spontaneously but burns with a grayish-blue flame to form arsenic trioxide. If the flame is extinguished, for example, by holding a cold porcelain dish in it, arsenic is deposited as a black patch. The pure gas is stable at normal temperature. If arsenic hydride is passed through a red-hot glass tube, it decomposes into hydrogen and arsenic (arsenic mirror), 185.1 kJ being released per mole of arsenic. The arsenic is deposited just behind the heated area as a bright, metallic black mirror (Marsh test). When treated with hypochlorite solution or with alkaline hydrogen peroxide solution, the patch changes into soluble arsenate. Arsenic hydride has a strong reducing action. It precipitates metallic silver from silver nitrate solution. It reacts with solid silver nitrate to form the yellow compound $\text{AsAg}_3 \cdot 3\text{AgNO}_3$ (Gutzeit arsenic test).

Arsine cannot be prepared by direct synthesis. The most convenient method of production is the reaction between sodium arsenide and water or zinc arsenide and dilute hydrochloric acid:



These reactions are fast and complete and have the advantage that the product is not contaminated with hydrogen. Arsenic hydride can also be produced by cathodic reduction or by reduction of arsenic compounds in acidic solution with zinc or magnesium. The last reaction is not quantitative because elemental arsenic, which does not react, precipitates. The product also has a high hydrogen content. Because arsenic is present as a common impurity in numerous metals suitable for the production of hydrogen, hydrogen produced by acid-metal reduction must be passed through a potassium permanganate solution to destroy any arsenic

hydride present. Particular practical significance is attributed to the formation of arsenic hydride in the pickling of metals when arsenic-containing sulfuric acid is used.

Arsenic hydride is so poisonous that a few inhalations of air containing arsenic hydride can result in death. The MAK is 0.2 mg/m³.

Arsenic hydride is used as a dopant in the semiconductor industry [41].

Arsenides. A number of arsenides occur in nature. Some have a defined composition, others are probably mixtures. Naturally occurring arsenides include Cu_3As (domeykite), FeAs_2 (löllingite), NiAs_2 (chloanthite), NiAs (niccolite), and CoAs_2 (smaltite). There are many minerals in which sulfur is partially replaced by arsenic.

The arsenides themselves have little commercial significance. Those produced are obtained by direct synthesis. The alkali-metal arsenides are also obtained by reaction in liquid ammonia. However, in this case polyarsenides can form in addition to the simple arsenides. The arsenides of the alkali metals, alkaline-earth metals, zinc, etc., are rapidly decomposed by water and acids with the formation of arsine. They may be regarded as derivatives of arsenic hydride. Most of the heavy metal arsenides, whose composition often does not reflect any simple relationship to arsenic hydride, are intermetallic phases and are highly resistant to acids. Gallium and indium arsenides are important in the semiconductor industry.

13.8 Uses and Economic Aspects

The demand for metallic arsenic is limited. It is used in nonferrous alloys, and high-purity arsenic is used in electronic and semiconductor devices. The addition of ca. 0.5% As to the lead grid in lead-acid storage batteries increases endurance and corrosion resistance. Additions of the same order to copper alloys improve high-temperature stability, recrystallization temperature, and corrosion resis-

tance. The addition of up to 2% As to lead used in shot improves its sphericity.

High-purity arsenic (at least 99.999%) is used in electronics in conjunction with gallium or indium for the production of diodes (LED), infrared detectors, and lasers. Solar cells based on gallium arsenide have an efficiency of 20% [42]. Commercial arsenic metal has a purity of 99%. Most arsenic is used in the form of compounds, arsenic trioxide being the sole starting material. Arsenic compounds are used in the following fields:

- Agriculture and forestry: herbicides and insecticides in cotton, coffee, and rice growing; wood preservatives; feed additives to aid in fattening and prevent infection
- Industrial chemicals: electrolyte purification in the electrolysis of zinc; metal pickles containing phosphoric acid
- Glass industry: fining agents and decolorizers [43]

Internationally, these fields of applications are all of importance; the regional differences are shown in Table 13.9 [44, 45], which also shows consumption figures for 1979.

The major producing countries for arsenic trioxide in order of capacity are Sweden, Mexico, France, the United States, the former Soviet Union, South-West Africa, and Peru. The principal manufacturers are:

Country	Manufacturer
France	Société minière et métallurgique de Pennaroya; Mines et Produits chimiques de Salsigne
Mexico	Industrial Minera Mexico SA (IMM)
Peru	Centromin-Peru (Empresa minera del centro de Perú)
South-West Africa	Tsumeb Corporation Ltd.
Sweden	Boliden Metall AB
USA	ASARCO Inc.
Former USSR	State-run companies

Production information is limited. The report of the Bundesumweltamt (Federal Department of the Environment, Germany) [45] based on a Bureau of Mines report [46] quotes a world production of 60 000 t for 1974. FRIEDENSBURG [47], in a world production

analysis (Table 13.10), arrives at only half that figure; however, that table only covers the ores smelted in the producing country.

Table 13.9: Arsenic consumption in tons of As_2O_3 content per year in 1979.

	United States		Former Fed. Rep. of Germany	
	t/a	%	t/a	%
Agriculture and forestry	13 500	70	0	0
Industrial chemicals	4 000	20	290	37
Glass industry	960	5	300	38
Alloys and electronics	600	3	171	22
Others (pharmaceuticals, catalysts, feed additives)	360	2	30	4
Total	19 420		791	

The world production of arsenic trioxide has been falling steadily since 1974. Production in Sweden and South-West Africa has declined to less than half. Because arsenic trioxide is a by-product, production is determined not by the demand for arsenic but by the demand for copper, lead, etc.

The biggest consumers of arsenic trioxide are the United States, Malaysia, and the United Kingdom, in that order. Malaysia uses arsenic-based herbicides in its rubber plantations; the United Kingdom imports As_2O_3 and

exports arsenic-containing pesticides and wood preservatives [44].

Storage. Arsenic trioxide is marketed as a bulk product packed in casks. Since arsenic compounds are classified as dangerous goods, all containers and shipments must be identified [48].

13.9 Safety Measures

Although pure metallic arsenic is not poisonous, the occurrence of toxic arsenic oxides formed by oxidation in air is unavoidable. In handling or manufacture of arsenical materials, inhalation of dust and skin contact with arsenic-containing gases must be prevented. In the absence of adequate safety measures the following jobs involve a risk:

- Metal recovery/contamination by arsenic
- Roasting of iron pyrites
- Cleaning of lead chambers in the manufacture of sulfuric acid
- Processing of arsenical minerals
- Production of arsenic-containing pharmaceuticals
- Use in pyrotechnics
- Burnishing of metal surfaces

Table 13.10: Arsenic production in tons of As_2O_3 content per year.

	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978 ^a	1979
Europe	42 780	38 127	19 868	16 344	16 659	16 790	16 770				22 189	
Germany	800	588	370	36	445	470	450				563	
France	13 600	13 600	10 191	8 022	9 000	9 000	9 000				7 280	
Portugal	200	247	190	186	14	20	20				—	
Sweden	21 050	16 500	2 000	1 000	—	16 525	—				6 706	
Spain	130	92	17	—	—	—	—				—	
USSR ^b	7 000	7 100	7 100	7 100	7 200	7 300	7 300				7 640	
Asia (Japan)	686	580	883	956	427	500	500				551	
SW Africa	484	2 217	4 062	3 700	2 370	8 140	8 000				2 407	
America (except USA)	15 380	8 934	10 272	12 330	6 306	5 548	5 050				—	
Brazil	312	300	298	148	164	69	50				—	
Canada	314	154	64	45	27	—	—				72	
Mexico	13 528	8 000	9 138	11 481	5 096	4 379	4 000				6 263	
Peru	1 226	480	772	656	1 019	1 100	1 000				1 257	
Total	59 330	49 858	35 085	33 330	25 762	30 978	30 320	—	—	—	32 739	
World (Bureau of Mines, [44])		63 945	65 263	62 029	58 557	59 994	59 395	51 971	42 989	38 918	40 283	40 475

^a From [44].

^b Estimated.

- Use of arsenic-containing raw materials in the glass industry
- Repair or cleaning of flue-dust plants, filters, etc.
- Use in wood preservatives.

All working involving arsenic or its compounds should be carried out in sealed containers. In filling and emptying of apparatus, adequate measures must be taken to ensure that the maximum allowable concentrations (MAK values) are not exceeded. A dust-free working environment should be ensured by maintaining reduced pressure in the apparatus or by an adequate exhaust system.

Sampling must be carried out only with the aid of suitable equipment, e.g., air locks, vacuum injectors, and sealed sampling vessels. Rooms used for work involving arsenical materials should be adequately ventilated and dust free. If there is a general danger of inhaling arsenical materials, e.g., during open sampling, respirators must be worn. In relatively heavily dust-laden atmospheres, special protective clothing should be worn to prevent any skin contact with arsenic. The arsenic content in the air of the working environment should be monitored continuously.

The MAK for AsH_3 in air is 0.2 mg/m^3 [50]. In Germany, arsenic trioxide, arsenic pentoxide, arsenous acid, arsenic acid, and their salts are included in the list of carcinogenic working materials. As a result a standard concentration of 0.2 mg/m^3 is stipulated for all arsenical compounds in Germany [49].

In Germany, all work involving arsenic and its compounds is governed by the regulations for dangerous materials (TRgA) [49]. Emphasis should be placed on personal hygiene, e.g., on the banning of eating and smoking in workrooms, on the need to wash before eating, and on the need to shower after finishing work. Adopting these measures can ensure a high level of occupational hygiene, even where work involving arsenic is carried out on an industrial scale.

In every country there are special provisions for packaging, identification, storage, and transportation of arsenical products. The

dangers involved in the use of arsenical preparations are not treated as seriously in the United States as in the EEC, where generally speaking such preparations are completely banned.

13.10 Toxicology

Nearly all arsenic compounds are considerably toxic, especially the inorganic ones.

The trivalent arsenic compounds, such as arsenic trioxide, As_2O_3 , arsenic trifluoride, AsF_3 , arsenic trichloride, $AsCl_3$, and arsine, AsH_3 , are markedly more toxic than the pentavalent compounds. Elemental arsenic itself is not appreciably toxic, but it is converted readily to toxic compounds in the organism. Pure arsenic(III) sulfide, As_2S_3 , also seems to have a comparatively low toxicity, but often the crude sulfide is contaminated by arsenic trioxide. In contrast, some pentavalent organic compounds have been used as therapeutics; these benzenearsonic derivatives contain a stable carbon-arsenic bond and are practically not converted to inorganic arsenicals [51].

Absorption. Arsenicals can be absorbed mainly by ingestion and inhalation, and also through the skin. They are widely distributed within 24 h into different tissues, mainly the liver, kidney, lung, spleen, bone marrow, skin, and, to a lesser extent, brain, heart, and uterus. Small quantities can be detected in hair and nails several months after the main portion of the arsenic has been eliminated from the body [52]. Inorganic arsenicals do not cross the blood-brain barrier but can pass across the mammalian placental membrane [53].

Excretion of arsenicals occurs mainly via urine, to a smaller extent via the feces [54], and by loss of hair and skin shedding. After the administration of a single dose, the concentration of arsenic in liver and kidney starts to decrease only after 24 h [54]. The concentration of arsenic in urine of unexposed persons is between zero and 0.22 mg/L , after industrial exposure between 0.04 and 0.9 mg/L [55]. After inhalation of arsenic dust, the excretion of methylated arsenic could be ob-

served [56]; traces of arsenic can be exhaled as trimethylarsine [57].

Metabolism. Most arsenic compounds – trivalent or pentavalent, inorganic or organic – are transformed to an arsenic oxide form, which can react readily with proteins, especially with those containing two vicinal mercapto groups, thus forming stable cyclic structures. The inhibition of essential enzymes is considered to be the first step of cell damage [51]. The high affinity of the arsenoxide moiety to the vicinal mercapto groups of 2,3-dimercapto-1-propanol (BAL, British Anti Lewisite) and of 2,3-dimercapto-1-propane-sulfonic acid is used successfully in arsenic poisoning therapy.

Arsenicals can cause acute, subacute, and chronic poisoning. However, acute poisoning is currently rare in comparison to subacute or chronic poisoning.

Acute Toxicity. Arsenic poisoning mostly occurs by ingestion of inorganic trivalent compounds such as arsenic trioxide. The smallest doses of As_2O_3 reported to be fatal after ingestion are 70–180 mg [52]. Symptoms which can occur within a few minutes or after a delay of several hours are vomiting, diarrhea, damage of the intestinal tract, muscular cramps, facial edema, cardiac abnormalities, dehydration, and – as a consequence – shock. The inhalation of irritant arsenic compounds, such as arsenic trichloride or arsenical war gases, causes cough, dyspnea, pain in the chest, severe damage to the respiratory tract, headache, general weakness, nausea, vomiting, and colic diarrhea. Airborne dusts often result in irritation of exposed skin and mucous membranes such as bronchitis, conjunctivitis, laryngitis, and dermatitis [58]. Arsenic trichloride may be absorbed through the skin with fatal consequences [59].

Chronic Toxicity. Chronic arsenic poisoning can be caused by intake of food and water contaminated with arsenicals or by inhalation of air-borne dusts during long-term occupational exposure, mainly in smelting plants of ores containing arsenic, insecticide factories, and

among vineyard workers, even many years after termination of exposure. Symptoms of these chronic poisonings were symmetrical palmar and plantar hyperkeratosis, white striae of the finger nails, cardiovascular manifestations, myocardial ischemia, hypertension, liver dysfunctions, hematological changes, and vascular disorders resulting in gangrenes of the lower extremities (blackfoot disease). A variety of severe symptoms is treated below.

Skin lesions are frequently observed, e.g., in the production of insecticides [60] and in copper ore smelting plants [61]. Typical symptoms are hyperkeratosis, warts, melanosis, contact dermatitis, eczematoid features of varying degrees of severity, and vascular lesions. Hyperkeratosis often is characterized by thickening, drying, and cracking of the skin [62]. Arsenical melanosis is also a common sign after long-term exposure and can occur on the chest, abdomen, scrotum, and back. Further characteristic symptoms are depigmentation (leukoderma) of pigmented areas and white striae of the fingernails [63].

Effects on mucous membranes are conjunctivitis with swelling and pain, keratoconjunctivitis (resulting from exposure to the insecticide calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$), irritation of the pharynx and bronchial passages, and irritation of the nose resulting in acute and chronic rhinitis. Among copper smelter workers, perforation of the nasal septum has been commonly observed [64].

Peripheral neuritis, with such symptoms as pain, difficulties in walking, burning and tenderness in the affected limbs, and later on severe weakness in both legs and feet, has been described after long-term exposure to arsenate dusts [62]. In contrast to the peripheral neuritis caused by lead, the arsenic-caused neuritis is painful; the nerves of these patients show neuronal degeneration [52]. Further symptoms, observed especially in cases of severe chronic intoxications, are headache, aphasia, drowsiness, disorientation, and changes in the personality.

Liver damages, especially liver cirrhosis, have been observed, e.g., in vintagers who used arsenical herbicides [65] and after long-

term consumption of arsenic-contaminated homemade wine [66]. These liver disturbances, which often are complicated by the additional occurrence of chronic hepatitis, ascites, and enlarged liver, are probably not due to skin contact with or inhalation of arsenicals, but to ingestion of contaminated wine. The occurrence of liver damage among industrial workers is reported to be less frequent [58].

Circulatory system symptoms after chronic arsenical poisoning are abnormalities in the electrocardiogram [67] indicating a toxic myocardial effect, peripheral vascular disturbances, gangrene of the extremities, atrophic acrodermatitis, endoangitis [68], and the so-called blackfoot disease [69].

Gastrointestinal disturbances are less common among workers with long-term exposure to arsenicals [70]. During chronic intoxication by ingestion, digestive disturbances, nausea, vomiting, and loss of appetite are occasionally reported.

Hematological changes are also less common in chronic poisoning after industrial airborne exposure. Symptoms like moderate anemia, leucopenia, and thrombocytopenia have been observed after long-term ingestion of inorganic arsenicals. However, these symptoms disappeared 2–3 weeks after termination of the arsenic ingestion [71].

Cancer. Workers in smelters or in insecticide factories exposed to arsenic trioxide have a significantly higher risk of lung cancer in comparison to persons not exposed [72, 73]. A significant excess of oral and pharyngeal cancer could be noticed among male textile workers in England and Wales engaged in fiber preparation [74]; this excess could be traced to arsenic-containing disinfectants used on sheep. Skin cancer as a result of ingesting of contaminated water, with multifocal lesions over the entire body, occurred in Cordoba, Argentina [75], Antofagasta, Chile [76], and in Taiwan [77]. The development of other types of tumors related to long-term exposure by ingestion, inhalation, or dermal contact has been observed frequently; however, in these cases the relationship between arsenic exposure and

development of tumors could not be confirmed as yet unequivocally [55].

Mutagenicity. The mutagenic action of inorganic and organic arsenicals has been tested on microorganisms (DNA damage in *Bacillus subtilis*) [78], *Drosophila* (increase in crossing-over frequencies) [79], and mammalian cells in vivo and in vitro. A significant increase of chromosomal aberrations could be demonstrated as a result of contact with arsenicals in lymphocytes from peripheral blood [80] and in fibroblast cultures of humans [81].

Teratogenicity. Teratogenic effects of disodium arsenate, such as exencephaly [82], cleft palate and lip, microanophthalmia, genitourinary abnormalities, ear deformities, and renal agenesis, were observed in hamster fetuses [83–85]. In the case of a 17-year-old girl, the ingestion of arsenic during the third trimester of her pregnancy caused the death of her baby (1100 g!) 11 h after birth; liver, kidney, and brain of the baby contained high concentrations of arsenic [86]. Among employees and persons living near a smelter, a significant decrease of the birth weight of the offspring, an increased frequency of spontaneous abortions, and a higher rate of malformations of the children born were observed [87, 88].

Arsine. Acute poisoning with arsine, AsH_3 , which is rather frequent among industrial workers as compared to poisoning with other arsenicals, results in general malaise, nausea, vomiting, abdominal cramps, coppery skin pigmentation, red staining of the conjunctiva [89], and leucocytosis [90]. A most characteristic symptom of acute arsine poisoning is rapid hemolytic anemia, which results in hemoglobinuria, decreased hemoglobin level, jaundice, and after 2–24 h, shock, oliguria, and anuria due to blockade of renal tubuli [91] by membrane residues of red blood cells. Other symptoms are pyrexia, edema of the lungs, delirium, and coma. Death after few days is mostly due to myocardial failure. In all cases of arsine poisoning an elevation of the T-wave in the electrocardiogram can be noticed. Depending on the severity of the intoxi-

cation, the time of the appearance of symptoms may vary between a few minutes and 24 h.

Chronic arsine poisoning shows a delayed onset of symptoms mentioned above, and in some cases peripheral neuritis [92], hemoglobin levels as low as 32 g/L, and basophilic stippling of red blood cells [93] have been observed.

Toxicological Data and Exposure Limits. Toxicological data of commonly used arsenicals are summarized in Table 13.11. The MAK values for arsenicals such as oxides, arsenic acids, and their salts are not established because these compounds have been proved to cause malignant tumors in humans [107]. The MAK value of arsine is 0.2 mg/m³ (0.05 ppm) [107]. The TRK values (Technical Guideline in Germany) for all compounds with the exception of arsine is 0.2 mg/m³ (as As) [108]. In the USA, the permissible exposure limit at work for calcium arsenate is 1 mg/m³, for arsine 0.2 mg/m³, for all other inorganic arsenic compounds 0.01 mg/m³, and for organic arsenicals 0.5 mg/m³ (as As) [109]. In Japan, the maximum allowable workplace air concentration for arsenic trioxide is 0.5 mg/m³, and for arsine 0.2 mg/m³ [110]. In Sweden, this value

is 0.05 mg/m³ (as As) for all arsenic compounds [111].

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Table 13.11: Toxicological data of arsenic and some arsenic compounds.

Compound	Toxicological parameter	Dose	Species	Route	Reference
Arsenic	LDLo	20 mg/kg	rat	intramuscular	[94]
Arsenic acid, hemihydrate	LD ₅₀	6 mg/kg	rabbit	i.v.	[95]
Arsenic pentoxide	LD ₅₀	55 mg/kg	mouse	oral	[96]
Arsenic trichloride	LDLo	100 mg/m ³ , 1 h	cat	inhal.	[97]
Arsenic trifluoride	LDLo	2000 mg/m ³ , 10 min	mouse	inhal.	[98]
Arsenic trioxide	LD ₅₀	45 mg/kg	mouse	oral	[96]
	LD ₅₀	20 mg/kg	rat	oral	[99]
	LDLo	4 mg/kg (as As)	rabbit	i.v.	[95]
Arsine	TCLo	3 mL/m ³	human	inhal.	[52]
	LCLo	25 mL/m ³ , 30 min	human	inhal.	[100]
	TCLo	93 µL/m ³	human	inhal.	[101]
Calcium arsenate	LDLo	50 mg/kg	rabbit	oral	[102]
Disodium arsenate	LDLo	30 mg/kg	rat	i.p.	[103]
Disodium arsenate, heptahydrate	TDL ₀	43 mg/kg	mouse	i.p.	[104]
Lead arsenate	LD ₅₀	100 mg/kg	rat	oral	[105]
	LDLo	75 mg/kg	rabbit	oral	[102]
Sodium metaarsenite	TDL ₀	40 mg/kg	mouse	oral	[106]

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14 Antimony

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14.1 Introduction

Antimony is an element of main group V having atomic number 51 and atomic mass M_r 121.75. Two isotopes occur in nature, mass numbers 121 and 123. The configuration in the outer electron shell is $5s^2 5p^3$. If these electrons are donated, antimony is electropositive and trivalent, as in SbCl_3 , or pentavalent, as in SbCl_5 ; if three electrons are added to the outer shell, the antimony is electronegative and trivalent, as in SbH_3 .

Usually antimony is a white lustrous metal of average hardness, 3.0 on the Mohs scale. It is brittle and easy to pulverize. If it solidifies slowly, pure antimony has a foliated structure; if rapidly, a granular structure. It forms rhombohedral crystals.

Metallic antimony is the only stable allotope. There are unstable forms: yellow antimony, black amorphous antimony, and what is known as explosive antimony. Yellow antimony is formed when air or oxygen is passed through liquid stibine. Black amorphous antimony is obtained by rapidly cooling antimony

vapors and is also formed from yellow antimony at -90°C . At room temperature black antimony slowly reverts to metallic antimony, and at 400°C reversion is spontaneous. Black amorphous antimony ignites spontaneously in air. Explosive antimony is obtained by electrolysis of antimony(III) chloride solution in hydrochloric acid at a high current density with an antimony anode and a platinum cathode. It consists of black amorphous antimony contaminated with antimony trichloride.

14.2 History

Antimony was known to the Chinese 5000 years ago. The ancient Egyptians were also acquainted with it, but they considered it to be a variety of lead, a belief that persisted until the 16th century. The first instructions on processing the Latin *stibium* or the Egyptian *stim* (antimony glance or stibnite) appeared at the beginning of our era. PEDANIOS DIOSKORIDES and PLINY THE ELDER referred to antimony glance as platyophthalmion (eye dilator), calliblephary (eyelid cosmetic), and gynaikeios

(feminine), because antimony(III) sulfide powder was then an ophthalmic ointment and a coveted cosmetic.

The word *Antimonium* seems to have been first used for antimony(III) sulfide in 1050 by CONSTANTINUS AFRICANUS. Light was gradually shed on the chemistry of antimony and on antimony therapy by PARACELUS (1526–1541), ANDREAS LIBAVIUS (*Alchemia*, 1597, and the *Syntagmatis Arcanorum* volumes, 1613–1615), the Benedictine monk BASILIUS VALENTINUS (*Triumphwagen Antimonii*, 1604), N. LEMERY (*Traité de l'antimoine*, 1707), and other works of the iatrochemical epoch. At an early stage, alchemists understood the significance of antimony for separating gold from silver. The recovery of *antimonium crudum* from its ores was described in detail by LAZARUS ERCKER (1574) and GEORGIUS AGRICOLA (*De re metallica*, 1556).

14.3 Properties

Density	
solid at 20 °C	6.688 g/cm ³
liquid at 630.5 °C	6.55 g/cm ³
Melting point	630.5 °C
Heat of fusion	10.49 kJ/mol
Boiling point at 101.3 kPa	1325 °C
Tensile strength	10.8 N/mm ²
Modulus of elasticity	566 N/mm ²
Surface tension	
solid at 432 °C	317.2 mN/m
liquid at 630 °C	349 mN/m
liquid at 1200 °C	255 mN/m
The surface tension of the solid decreases nearly linearly with temperature. The slope at the melting point is $-0.07 \text{ mNm}^{-1}\text{K}^{-1}$	
Molar heat capacity at 630.5 °C	
solid	30.446 Jmol ⁻¹ K ⁻¹
liquid	31.401
Coefficient of linear expansion between 0 and 100 °C	$10.8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$
Thermal conductivity	
at 0 °C	18.51 Wm ⁻¹ K ⁻¹
at 100 °C	16.58

Roughly 1/20th of the thermal conductivity of copper. The thermal conductivity of antimony depends on the grain size and the direction in the crystal.

Electrical resistivity at 0 °C	$30.0 \times 10^{-6} \text{ } \Omega\text{cm}$
Molar susceptibility at 20 °C	-99.0×10^{-6}

Polycrystalline antimony is diamagnetic.

Pure antimony does not change in air at room temperature, and it is not tarnished in humid air or pure water. If antimony is heated to redness in air, the molten metal ignites. Above 750 °C, steam oxidizes liquid antimony to antimony trioxide, and hydrogen is evolved. Antimony can be removed from lead–antimony alloys with steam. Antimony cannot be ignited in a current of hydrogen. If it is heated to redness in a current of nitrogen, gray vapors are given off, which condense to amorphous antimony.

Neither solid nor liquid antimony dissolves nitrogen. Fluorine, chlorine, bromine, and iodine react violently with antimony, even at room temperature, to form trihalides. The reaction with chlorine yields either SbCl₃ or a mixture of SbCl₃ and SbCl₅. Antimony(III) sulfide is the product of the reaction with sulfur, hydrogen sulfide, or dry sulfur dioxide. In the presence of an oxidizing agent or sulfur, aqueous sodium sulfide dissolves antimony to yield sodium thioantimonite. Yellow ammonium sulfide and sulfur-containing potassium sulfide solutions also readily dissolve antimony.

Molten antimony reacts with phosphorus, arsenic, selenium, and tellurium but not with boron, carbon, and silicon. The eutectic with lead contains 13% antimony and melts at 246 °C.

Antimony is resistant to concentrated hydrofluoric, dilute hydrochloric, and dilute nitric acids. It is readily soluble in a mixture of nitric and tartaric acids and in aqua regia. Phosphoric acid and a few organic acids also dissolve the metal, although acetic acid hardly belongs to this category. At room temperature it is not attacked by dilute or concentrated sulfuric acid. It is attacked at 90–95 °C by concentrated sulfuric acid, and sulfur dioxide is evolved.

Pure antimony is resistant to solutions of ammonium and alkali-metal hydroxides and to molten sodium carbonate. If heated to redness, it reacts with molten sodium or potassium hydroxide to form hydrogen gas and antimonites.

In the electrochemical series antimony falls between hydrogen and bismuth: H, Sb, Bi, As, Cu.

14.4 Occurrence

The average antimony content of the earth's crust has been estimated at $3 \times 10^{-5}\%$. Most antimony lodes occur in areas of volcanic activity and frequently in volcanic rocks themselves. They are found predominantly in ancient formations ranging up to the Carboniferous. Antimony deposits are seldom of sedimentary or epigenetic origin.

The most important antimony ore is rhombic *antimony glance* (gray antimony, antimonite, or stibnite), Sb₂S₃. It contains 71.7% antimony and occurs as characteristic black acicular crystals. Other ores include antimony oxides (valentinite, Sb₂O₃, rhombohedral; senarmontite, Sb₂O₃, cubic; cervantite, Sb₂O₄, orthorhombic), antimony hydroxides (stibiconite, Sb₂O₄·H₂O), antimony oxide sulfides (kermesite, pyrostibite, red antimony, 2Sb₂S₃·Sb₂O₃), native antimony, and double sulfides (jamesonite, Sb₂S₃·2PbS, which may contain silver, tetrahedrite, Sb₂S₃·4Cu₂S₂; and livingstonite, 2Sb₂S₃·HgS). More than 100 minerals containing antimony are known: there are eight antimonides, one sulfide (stibnite), 59 mixed antimonides and sulfides, and 46 oxide minerals.

Other sources of antimony besides ores are the intermediates in the processing of lead ores and the copper ore tetrahedrite, including the dross and slags from lead refining (particularly in the Harris process), speiss, flue dust, and anode slime.

Until about 1930, *deposits* in China supplied 70% of the world production of antimony ores. These were mined in Ksikwangshan (Hunan) and the provinces of Kwangsi Chuang, Kwangtung, and Yunnan. Now China's contribution has dropped to 16%, and China is only the third largest producer. Since the mid-1970s, Bolivia has been the largest producer of antimony ores, accounting for about 25% of the world total. The

production figures were 13 019 t in 1979, 17 092 t in 1980, and 15 296 t in 1981. The regions in which the ores are mined are San Juan, Tubiza (near Atocha), Huari, and Uncia. The second largest producer is South Africa (Murchison Range), accounting for an average of 18% of the total.

The fourth largest is the former USSR (Chajdarkan and Kadam-Dzai in Central Asia and the Ural and Caucasus Mountains), accounting for about 10% of the world production. Significant amounts are produced in Mexico, Thailand, Canada, Yugoslavia, Australia, Turkey, Greece, Italy, Spain, Austria, the United States, Morocco, Guatemala, former Czechoslovakia, and Brazil. Today, about two thirds of the world production of antimony ores is mined in Western countries, the American continents alone accounting for 30–40%. Frequently, the recovery of lead, silver, and gold is the primary mining goal, with the antimony only a by-product. An exception is the Murchison Mine in South Africa.

14.5 Beneficiation

The beneficiation process used depends chiefly on the content of antimony and other substances in the ore. Another important factor is how the ores are dispersed in the rock. If an antimony ore is not closely interlaced with the gangue, hand-picking techniques or jigs suffice for separation.

If stibnite (Sb₂S₃) ore contains more than 90% stibnite, it can be sold directly as Sb₂S₃ (crude antimony). Stibnite has a low melting point, and it can be extracted by melting if the ore contains 45–60% antimony and is free from lead and arsenic. This technique is called liquation. If the antimony content lies between 5 and 25%, the antimony is concentrated in a flue dust by volatilizing roasting. Antimony ores may contain auriferous antimony sulfides and arsenopyrites. Beneficiating such ores may become profitable again because of their precious metal content.

As a rule, low-grade and complex ores or ores in which the minerals are finely dispersed

throughout the gangue are beneficiated by flotation, particularly if they contain precious metals [15–18].

Flotation. A run-of-mine ore containing about 0.5% arsenic in the form of auriferous arsenopyrites and 5–20% antimony in the form of antimonite can be floated in a pulp made strongly alkaline by potassium hydroxide or water glass. The flotation agent is often potassium xanthate, and a high selectivity is ensured by frothing agents, such as the synthetic foaming agent Flotol for arsenopyrites and dicesyl dithiophosphoric acid (Phosokreslo and Aerofloat) for antimonite [15].

Liquation. Ores with more than 40–60% Sb_2S_3 and free from lead and arsenic often are beneficiated by heating. Because stibnite, Sb_2S_3 , has an unusually low melting point, 546–548 °C, it can be separated from the gangue by melting (liquation). Stibnite more than 90% pure is obtained and is referred to as *crude antimony*. It can be sold as such for producing antimony compounds, or it can be converted to antimony metal.

The commercial product should have a striated crystalline structure and a metallic gloss, and its color should be that of graphite. These properties are attained only if the molten antimony(III) sulfide is cooled very slowly. Ores with less than 40–45% Sb_2S_3 are unsuitable for liquation because the large amount of gangue interferes and too much antimony is retained in the residue. The ore is best fed in the form of walnut-sized lumps (1–4 cm). If the ore is too fine, the molten Sb_2S_3 does not flow. The most suitable temperature range is 550–660 °C because the volatilization of the Sb_2S_3 (*bp* 1000 °C) is prevented, and liquation is successful. Liquation is carried out in a reducing atmosphere in crucibles or in reverberatory furnaces. The main impurities in crude antimony are arsenic, lead, and iron sulfide.

14.6 Recovery of the Metal

Antimony metal is recovered from ore primarily by pyrometallurgical techniques. Either antimony(III) sulfide is converted into the

oxide, which is then reduced, or the ore is partially roasted and allowed to react with sulfide to form the metal and sulfur dioxide.

Sulfide ores with antimony contents between 5 and 25% are roasted to give volatile Sb_2O_3 , which is reduced directly to the metal. In many smelters mixed oxide–sulfide ores are processed in water-jacketed furnaces together with recycled material and by-products containing antimony. Reverberatory furnaces are used mostly for reducing rich oxide materials. The most suitable processes are listed in Table 14.1 for the various oxide and sulfide ores.

Table 14.1: Suitable processes for various antimony ores or concentrates.

Nature of the ore	Antimony content, %	Process
Sulfide	< 20	volatilizing roasting
Sulfide	< 35	smelting in shaft furnaces
Sulfide	> 60	liquation and cyclone volatilizing
Oxide	< 30	smelting in reverberatory furnaces and shaft furnaces
Oxide	< 50	direct reduction
Mixed sulfide and oxide	—	smelting in shaft furnaces

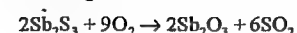
Special processes are used if the ore is rich in precious metals. Hydrometallurgical techniques can be used to minimize losses of precious metals. For example, crude metal is obtained at the cathode in a hydrometallurgical process used by the Sunshine Mining Co. (Cœur d'Alene district). Because rich ores are becoming rare, greater recourse is being taken to intermediates in processing and metal industries. Also, more and more complex ores are being processed.

14.6.1 Roasting

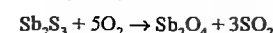
The sulfide can be oxidized to antimony(III) oxide (volatilizing roasting) or to antimony(IV) oxide (nonvolatilizing or dead roasting). Furnace control in the production of the nonvolatile antimony(IV) oxide is comparatively simple, but the oxide is not separated from the residue. If the ore contains a high proportion of gangue, difficulties are en-

countered in reduction. As a result this process is used rarely today.

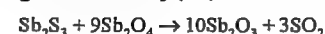
Volatilizing roasting has the advantage that volatile Sb_2O_3 is produced selectively in a 98% yield and is separated from the residue, which contains the precious metals in a recoverable form. However, temperature and draft control in the furnace is difficult. The oxide forms between 290 and 340 °C in an oxidizing atmosphere, and the rate of reaction attains its maximum at 500 °C, where antimony(IV) oxide begins to form. The basic reaction is



If too much oxygen is available, antimony(IV) oxide is formed:



Above 560 °C the rate of reaction drops considerably. During roasting, antimony(IV) oxide can react with antimony(III) sulfide to give antimony(III) oxide:



Therefore, the process must be engineered so that Sb_2O_3 is formed rapidly and preferentially. The temperature must be high enough to ensure adequate volatilization, and the oxygen supply must be kept low to inhibit the formation of antimony(IV) oxide. However, if the temperature is too high, part of the charge will melt, envelope the sulfide grains, and prevent their oxidation. During condensation of antimony(III) oxide, the oxygen content in the gas phase must be kept low enough to prevent oxidation to antimony(IV) oxide.

The temperature level is governed by the sulfide content of the ore. Low-grade ores can be roasted between 850 and 1000 °C. If rich ores are roasted, the upper limit is the melting point of the sulfide (546 °C). In practice, the temperature should not exceed 400 °C. The oxygen supply is controlled by mixing wood charcoal or coke breeze with the charge and by admitting only the amount of air required to form carbon monoxide and antimony(III) oxide. The carbon monoxide suppresses oxidation to antimony(IV) oxide. Despite everything, however, formation of antimony(IV) oxide cannot be entirely sup-

pressed. Antimony(IV) oxide, lead(II) oxide, and flue dust are obtained in the first condenser. The antimony(III) oxide condenses in the second, and the very volatile arsenic(III) oxide condenses in the last. If the oxygen concentration in the roaster is too low, partial oxidation can occur and give a mixture of oxide and sulfide melting at 485 °C. If the concentration of oxygen is too high, arsenates and antimonates of lead, copper, and other metals can form and pass into the slag.

A grain size of 5–10 cm suffices in conventional processes because fresh surface is always exposed for reaction owing to volatilization of the trioxide. Very low grade ores must be ground more finely to separate the sulfide from the gangue. The yield depends on the process and the sulfide content of the ore, varying between 60 and 90% or more.

Commercial antimony(III) oxide should be at least 99.5% Sb_2O_3 . If it is finely crystalline, adheres firmly to the fingers, and does not cake, it is considered of good quality. The oxide must be white; a reddish tinge indicates the presence of antimony(III) sulfide. The yellowish shade of selenium and lead(II) oxide is also undesirable. The arsenic content should be on the order of 0.1%. Typical specifications and grain size distribution [19] are listed below (in %).

Assay	99.5
Sb_2O_4	0.209
As_2O_3	0.11
PbO	0.15
Fe_2O_3	0.03
SeO	0.001
S	0.18
Solubility in tartaric acid	> 99.5
Solubility in water	< 0.4
Whiteness measured by reflectometry	> 90
Size distribution	
0–1.5 μm	60
1.5–3 μm	38
> 3 μm	2
> 44 μm	0.1
Apparent density	0.8 kg/L

The *roasting furnaces* most commonly encountered today are rotary kilns. If the throughput is high, antimony(III) oxide yields of 95–98% are attainable. The yield does not depend on the nature of the ore. The antimony content of sulfide ores does not affect the

kiln's efficiency; therefore, sorting and flotation of low-grade sulfide ores are unnecessary. Rotary kilns are also suitable for oxide sulfide ores, reducing the antimony initially to the metal. The metal volatilizes and is oxidized to antimony(III) oxide that is free of nonvolatile impurities and the off-gases produced on reduction. Some rotary kilns are heated not by burners but by hot air blown into them. The gas flow rate is significantly less than that in the old burner-heated furnaces, and less gangue is entrained in the gas stream. Nevertheless, hot-air heating does not entirely avoid temperature peaks, with melting of the charge.

Cyclone smelting entirely eliminates melting of the charge. The antimony smelter at Vinto, Bolivia, was the first in the Western Hemisphere to use the cyclone furnace smelting process. Conventional antimony roasting consumes large amounts of coal, and the lack of domestic coal has favored the cyclone furnace. The feed contains at least 60% antimony and less than 0.5% lead plus arsenic. Antimony is volatilized as antimony sulfide, burned, and separated in a baghouse as antimony(III) oxide. The impure oxide is pelletized and melted in a rotary furnace. The cyclone slag contains about 1% antimony [20].

14.6.2 Reduction of Oxide to the Metal

The oxides from volatilizing roasting, as well as other oxidized antimony materials, are reduced to the metal with carbonaceous materials. Occasionally oxide ores containing more than 50% antimony are finely ground and also reduced. Sometimes the oxide must be treated beforehand to remove arsenic, but improved roasting techniques frequently make this unnecessary. The amount of carbon required for reduction depends on the composition of the oxide, ranging between 8 and 12%. Pulverized charcoal, anthracite dust, or lean coal dust are used. To prevent the loss of volatile Sb_2O_3 , a sodium salt, such as soda (Na_2CO_3) or Glauber's salt (Na_2SO_4), is added to give a slag of low viscosity. Impurities such as cop-

per and iron are converted to matte by adding sulfur, usually in the form of crude antimony. The slags can contain 5–20% antimony, which must be recovered. The oxides are reduced in shaft, reverberatory, or short rotary furnaces. All types of furnaces require efficient precipitators and off-gas filters to remove volatilized antimony(III) oxide.

The pronounced reducing action in shaft furnaces does not produce pure metal but does yield slags containing a maximum of only 2.5% antimony and usually less than 1%. These slags can be used in glass manufacture. The furnaces have large height to diameter ratios, e.g., 6:1. The charge must be in the form of lumps or briquets. The yield is between 95 and 98%; the impure product contains 90–92% antimony, 5–7% iron, and arsenic and lead.

Reverberatory furnaces produce metal of comparatively high purity, but the slag is rich in antimony and requires further treatment. These furnaces are fed with high-grade ores that yield fairly small quantities of slag and with antimony-laden flue dust.

Stationary reverberatory furnaces have been largely replaced by *short rotary furnaces* in which the charge is very thoroughly mixed and rapidly melted. The rotary movement efficiently transfers heat to the charge. Tapholes are arranged at various heights in the furnace to allow molten metal, liquefied slag, and solid residues to be withdrawn. The great advantage of this process is that reduction in the furnace can be controlled so that the accompanying metals, such as lead, iron, and arsenic, are not reduced or are volatilized. This makes the refining simpler. At the antimony smelter at Vinto, Bolivia, the oxide melt passes from the rotary furnace to reverberatory furnaces for reduction and final refining at 800 °C. Coal and sodium hydroxide are added. The final product contains 99.6% antimony. If less pure, it can be alloyed with copper, nickel, or lead. The total antimony recovery rate for the smelter is 92% [20].

The complete flowsheet is shown in Figure 14.1.

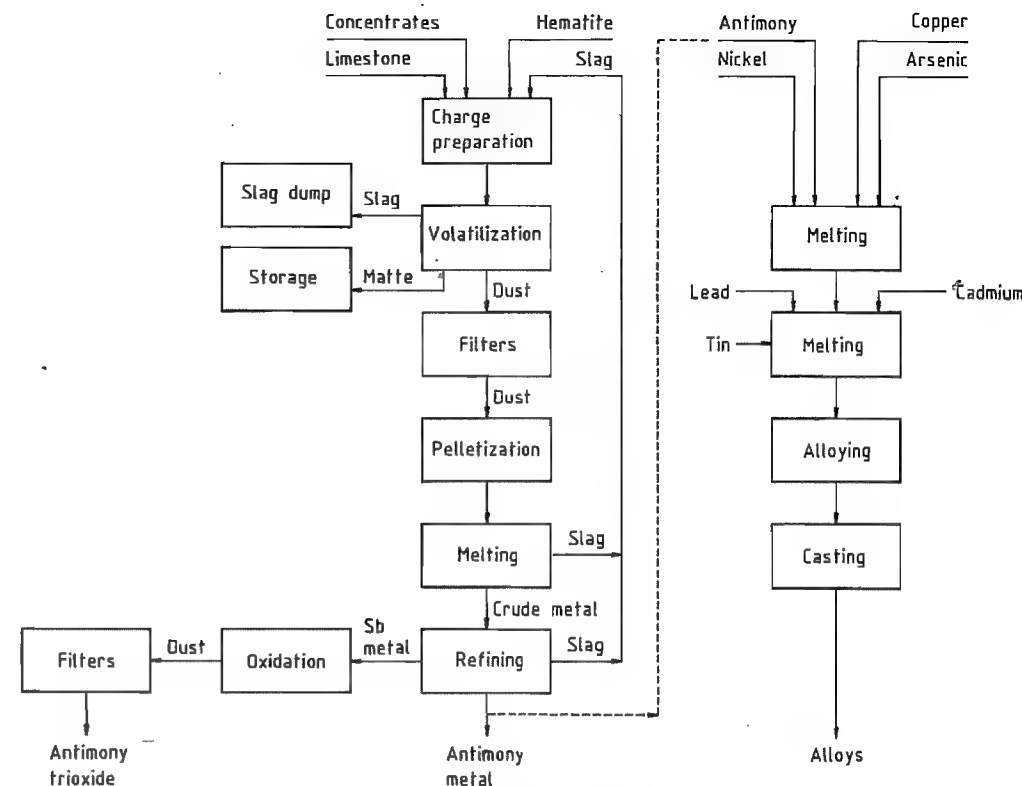
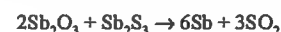


Figure 14.1: Antimony flowsheet for the smelter at Vinto, Bolivia [20].

14.6.3 Direct Reduction to the Metal

In blast furnace smelting the charge is antimony(III) sulfide, either alone or mixed with antimony oxides. The molten sulfide is first oxidized by the air blast. The oxide formed reacts with unconverted sulfide to yield metallic antimony.



In view of the many oxidation states through which the antimony must pass, this process is undoubtedly more complex than the equivalent lead and copper processes. It has been successfully practiced for many years in Mexico, Belgium, Great Britain, and former Czechoslovakia. Best results are obtained with sulfide ores containing 25–30% antimony. The main disadvantage of the direct process is

that antimony compounds are volatilized; this has been offset by using high, slender smelting columns.

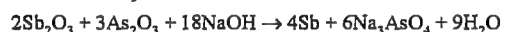
Standard practice favors low air pressures, e.g., 5.5 kPa at a flow rate of 1200 m³/s. The antimony content of the mixed charge should be less than 20%. Suitable fluxes are limestone, pyrite cinders, and ferrous slags. The required proportion of coke is about 15%. The slag and the metal usually are separated in a heated forehearth.

The yield of antimony can be as high as 98%, but not all of this is metal. Some leaves the shaft furnace as oxide, which must be trapped in filters. The metal is contaminated by iron, lead, and some copper and arsenic and must be refined.

14.6.4 Other Direct Processes

Reduction smelting of sulfidic antimony ores together with alkaline slags is a standard, long-established practice. A charge containing 8% sodium carbonate, 4% sodium sulfate, and 8–12% coal, for example, is smelted in a short rotary kiln. The alkaline melt absorbs the sulfur, so the metallic antimony produced must be refined.

Smelting antimony oxide flue dust containing arsenic, such as is obtained in roasting ores, with sodium hydroxide produces metallic antimony.



The arsenic dissolves in the alkaline slag [21–23].

14.6.5 Hydrometallurgical and Electrolytic Methods

Hydrometallurgical processing is suitable for some ores, particularly those containing gold, silver, and copper, and especially tetrahedrite, $\text{Sb}_2\text{S}_3 \cdot 4\text{Cu}_2\text{S}$ [24–27]. The high antimony content makes extracting the precious metals with cyanide difficult.

A number of methods have been proposed; however, most are plagued by unresolved problems. If sulfidic antimony ores are digested with acids, hydrogen sulfide is given off. Sulfuric acid does not digest the ores completely at 300 °C. Although hydrochloric acid is a better solvent and the antimony(III) chloride is adequately soluble, the problems involved in further processing have not been resolved. Cementation with iron, precipitation as the sulfide, and electrolysis have been investigated as means of separating the antimony. Explosive antimony is likely to form if electrolysis is used on antimony chlorides.

Antimony ores can be digested by *alkalies*. The antimony then can be reduced from the solutions electrolytically or by cementation with aluminum or zinc. Very pure rhombohedral antimony is obtained by electrolysis.

Any raw materials that are soluble in sodium sulfide, e.g., antimony glance or foundry products containing antimony sulfide, are suit-

able starting materials for antimony recovery by electrolysis. The solution is purified and then electrolyzed in diaphragm cells with iron or lead anodes and iron cathodes. The purity of the antimony is 96–99%.

The source of all the valuable metals in the Sunshine Mine ore is an argentiferous tetrahedrite (a silver copper–antimony sulfide), which cannot be broken down physically into its constituents. The tetrahedrite occurs reasonably free, and about 85% can be floated into a high-grade concentrate after grinding to a relatively coarse size.

The high antimony content precludes adoption of large-scale copper smelting for the concentrate, and lead smelting is just as unsuccessful because of the high antimony and copper contents and the presence of bismuth. Instead, the antimony is extracted from the argentiferous tetrahedrite by an alkaline sulfide solution. The residue consists of insoluble silver and copper sulfides. The antimony is recovered from the alkaline solution by electrolysis.

The steps are as follows:

- The antimony is batch leached with hot concentrated sodium sulfide solution from milled tetrahedrite concentrate to give a solution containing about 250 g Na_2S and 50 g Sb per liter. The leaching time is 8–10 h at 100–103 °C.
- After the residue settles, the supernatant solution is decanted. The residue is recovered by two-stage filtration with a repulping step between the stages. The pregnant solution is fed to the electrolytic section through two anolyte and two catholyte tanks.
- The solution is batch electrolyzed in banks of diaphragm cells. The antimony is deposited at mild-steel cathodes. The electrolytic section consists of 96 cells in series, arranged in cascades of six.

During electrolysis, the antimony is deposited at the cathodes, and sulfur is concentrated in the anolyte, with the result that sodium polysulfide (Na_2S_3), sodium sulfite (Na_2SO_3), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), and sodium sulfate (Na_2SO_4) form. The alkalinity of the

anolyte decreases, whereas that of the catholyte increases.

Fresh anolyte is made up from a mixture of caustic soda solution and barren catholyte to be equivalent to 225 g NaOH per liter. It is discharged into the anolyte feed tanks in 7.5-t batches, and the same volume, having an alkalinity of about 175 g/L, is withdrawn to the regeneration section.

The fresh catholyte, also handled in batches, carries about 50 g of antimony and the equivalent of 250 g of NaOH per liter.

Catholyte is introduced near the bottom of each cell and withdrawn at the top. Because antimony depletion lowers the specific gravity, the weakest solution is drawn off and fed to the following cascade. The solution leaving the final cell in a cascade is pumped back to the catholyte feed tank, unless its antimony content has been reduced to the barren solution level of 8–10 g/L. The barren solution has an alkalinity equivalent of ≈ 250 g NaOH per

liter. About 30 t of barren solution is withdrawn during each cycle, and the same amount of fresh pregnant solution is added to the feed tank.

The busbar current is 1500 A, producing a current density of 300 A/m². There is no gasing at the cathodes until the antimony content of the solution falls below 8 g/L. The voltage drop varies slowly between 2.5 and 3 V per cell, depending on the alkalinity of the anolyte, averaging about 2.65 V. The cathodes are stripped every three days.

The spent solution from both the catholyte and anolyte cell banks are led to the regeneration circuit for treatment with barium sulfide solution. After the precipitated barium salts have been separated, the solutions are returned to the leaching circuit. The precipitated barium salts are mixed with coal and passed through a rotary kiln for reduction to a black ash containing barium sulfide.

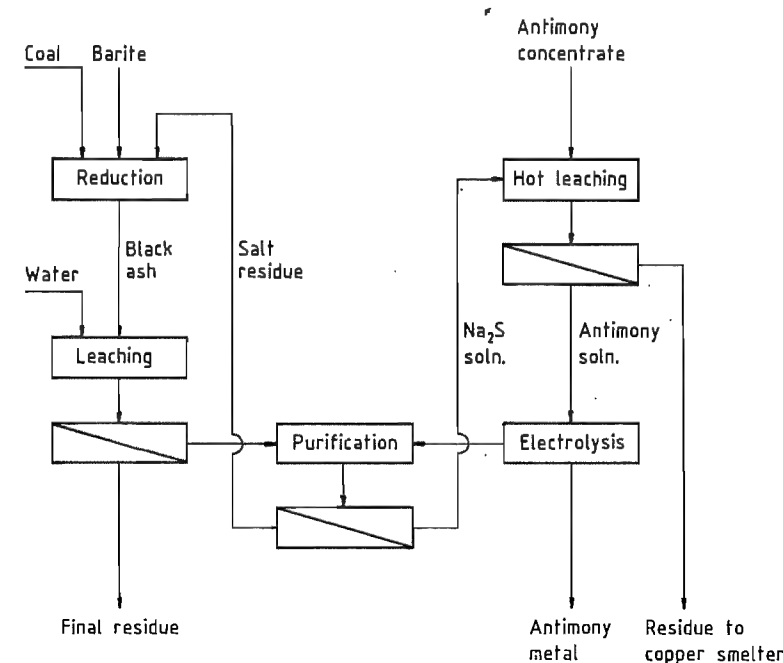


Figure 14.2: Flowsheet for the Sunshine electrolytic antimony plant.

The process is cyclic and regenerative, except that some barite must be supplied, and some caustic soda must be added to the anolyte to replace sodium lost with the copper residue. The antimony is sold as unrefined granular cathode antimony containing 96–97% antimony and 2–3% arsenic. Copper, lead, iron, bismuth, and other elements make up less than 0.4%. The small remainder is probably sodium sulfate. The flowsheet for the Sunshine Mining Co. electrolytic process is shown in Figure 14.2 [28].

In a method devised by the U.S. Bureau of Mines [29], the concentrate containing precious metals is smelted together with some iron. The metal obtained is deposited electrolytically at the cathode and refined. As much as 80–90% of the antimony is recovered as metal; 80–94% of the gold and 30–48% of the silver pass into the anode mud (Figure 14.3).

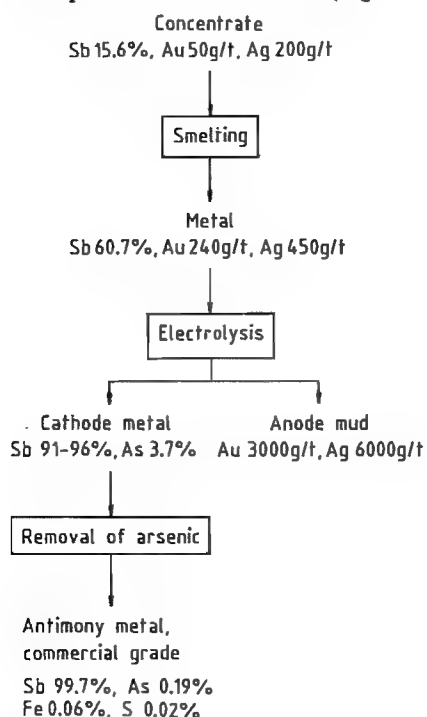


Figure 14.3: Beneficiation of a concentrate containing precious metals [29].

In another process the ore is smelted with soda and tetrahedrite and leached with lime.

The antimony passes into solution as sodium thioantimonate, Na_3SbS_4 . The arsenic is precipitated. If the ratio of sodium to sulfur in the electrolyte is 2:1 and the current density on the order of 1000 A/m^2 , no diaphragms are needed; the current efficiency is 60% [30].

14.6.6 Recovery from By-products, Complex Ores, and Recycled Material

Lead and copper ores often contain antimony, which is concentrated and removed during the recovery of the main metal.

In the pyrometallurgical processing of *antimony-containing lead ores* about 90% of the antimony is recovered in the lead. During refining, the antimony is oxidized, usually in reverberatory furnaces, into an oxide slag, called antimony skimmings. After the entrained lead has been liquated, skimmings are smelted together with coal and fluxes, frequently in short rotary kilns, to yield a crude antimonial lead.

In the Harris process, lead bullion is treated at 400°C with a melt of sodium chloride, sodium monoxide, and sodium nitrate. Arsenic, tin, and antimony are converted into a slag containing the antimony as sodium antimonate. Hydrometallurgical processing of the slag separates arsenic, tin, and antimony. The residue contains 45–50% antimony and can be reduced to antimony metal or used to produce antimony compounds.

In some cases electrolytic refining is used, particularly for lead rich in bismuth. The antimony is retained in the anode mud, together with the other undissolved metals – copper, arsenic, bismuth, and precious metals [31, 32]. The anode mud is smelted under reducing conditions to give a lead alloy. The arsenic and antimony are removed by selective oxidation at $900\text{--}1000^\circ\text{C}$ and converted into a slag in a procedure similar to that used in lead refining. The slag is smelted under reducing conditions to yield antimony containing arsenic.

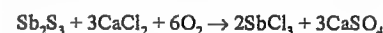
About 85–95% of the antimony in lead ores is recovered in the form of antimony–lead alloys, which are usually diluted with refined

lead and sold as is. These alloys are used mainly in lead–acid storage batteries.

In smelting *antimonial copper ores*, about 85% of the antimony enters the flue dust. The dust from the converter stage contains about 50% of the antimony, the arsenic, and frequently lead as well. The particular composition determines how these flue dusts are processed; there are no standard procedures. If iron, nickel, cobalt, arsenic, and antimony are present in sufficient amounts, they accumulate, together with the precious metals, in the copper matte during smelting. This speiss is difficult to process, and there is no satisfactory method that can be adopted generally.

Before *mercury-containing antimony ores* are processed, they generally must be roasted below 400°C to volatilize the mercury. The temperature must be controlled accurately by regulating the admission of air to avoid overheating the charge and thus volatilizing antimony compounds. The roasted ore still contains antimony sulfide. The ore is removed from the furnace special bunkers. The antimony is recovered by reduction or iron precipitation in open-hearth furnaces.

Another way to process *complex antimony sulfide ores* is reaction with calcium chloride. The reaction takes place in an oxidizing atmosphere at about 500°C :



More than 90% of the antimony volatilizes as SbCl_3 , which can be purified by distillation and hydrolyzed to Sb_2O_3 . The flow sheet is shown in Figure 14.4 [19].

The main forms of *antimony scrap* are type metal, Babbitt metal, lead and tin waste, antimonial lead, and especially waste lead–acid batteries: the recycling of antimony is closely connected to lead recycling. The extent to which antimony is recycled has increased steadily over the last few decades, in proportion to the worldwide production of automobiles.

Antimony accounts for about 1.8–2% of the total weight of an automobile battery, although the trend is towards using less. Today,

waste batteries are separated mechanically into a plastics fraction, a metal fraction, and an oxide–sulfate sludge. The grid metal contains 87–88% lead and 3–3.5% antimony; the sludge, 70–76% lead and 0.5–1% antimony. Most refineries process these materials separately from ore or concentrate. The waste grid metal can be smelted in rotating reverberatory or rotary kilns to yield antimony–lead alloy. The sludge is treated with reagents that bind sulfur, e.g., iron filings and soda, and smelted under reducing conditions to antimonial lead in rotating reverberatory furnaces, short rotating furnaces, or in some cases rotating tube furnaces. The antimonial lead produced can be remelted together with lead containing a higher proportion of antimony to produce commercial alloy. Frequently, the antimony in the crude antimonial lead is converted by oxidation into an antimonial slag or skimmings, as in the refining of lead bullion. These oxidized products, essentially lead and antimony, are treated with fluxes and coal and smelted in short rotating or rotating reverberatory furnaces to yield lead containing a high proportion of antimony. Because battery alloys now contain less antimony, the proportion of antimony in recycled lead will be lower in the years to come.

14.7 Refining

Antimony from the smelter usually contains iron, arsenic, tin, zinc, copper, lead, and bismuth. Several processes are used to produce a commercial grade containing $\geq 99\%$ antimony and $\leq 0.3\%$ arsenic. Iron, arsenic, and tin are removed by melting with caustic soda. A slow current of air is passed over the metal–caustic soda bath. Generally the caustic soda is renewed once during purification. At a bath temperature of 950°C and a total air flow of $500 \text{ m}^3/\text{kg}$ arsenic is reduced in two hours to a residual 0.05% and iron is reduced to a residual 0.005%. Sodium nitrate can be used instead of the combination of caustic soda and air.

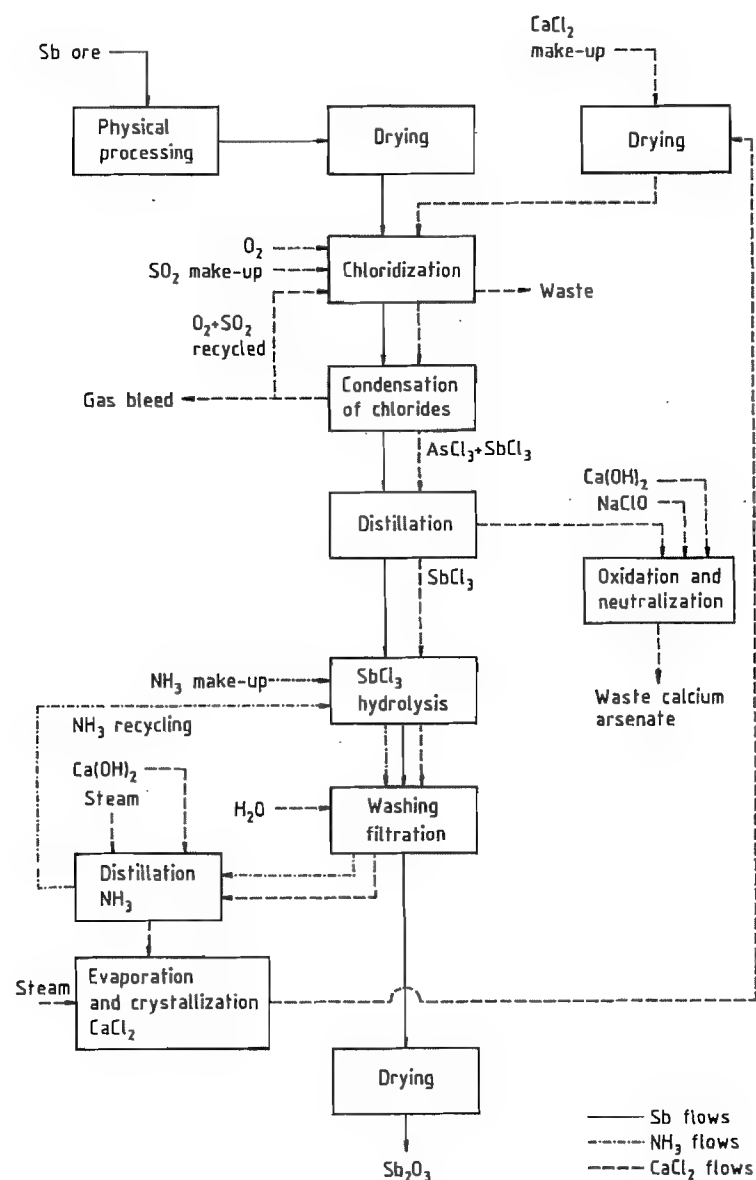


Figure 14.4: Chloridization process.

Although the maximum permissible arsenic content is 0.3%, a maximum of 0.1% is often specified. The measures taken to ensure such a low content must begin in the earliest beneficiation stages. The methods are well known, and some of them are standard practice [4, pp. 38–45].

To a great extent arsenic can be prevented by selective flotation from entering the concentrate [15, 33, 34]. About 88% of the arsenic can be volatilized from concentrates and antimony oxide flue dust by roasting in the presence of steam at 475–500 °C. The associated antimony losses are limited to 10–45%. If

arsenic antimony oxides are treated with hot caustic soda, the arsenic trioxide passes into solution as arsenite, whereas the antimony oxide is not changed. One to six kilograms of caustic soda is required for each kilogram of arsenic. The arsenic is completely separated from the antimony [4, p. 44].

Electrostatic precipitators offer means of separating arsenic from antimony at elevated temperature because gaseous arsenic trioxide can pass through them, whereas solid antimony trioxide precipitates. The best results, only 0.66–0.79% arsenic in the antimony trioxide, are obtained for a gas-inlet temperature of 620–650 °C and an outlet temperature of 430–470 °C.

The removal of lead from crude antimony is of less importance because most antimony produced is used in lead alloys. In any case, separation is difficult owing to the affinity between the two metals. Suitable methods are electrolysis, chloridization, and sulfidization.

A number of methods have been proposed, and occasionally used, for electrolytic separation of lead from antimony on an industrial scale [4, 24]. Although pure antimony is obtained from alkaline thioantimonite solutions, the current efficiency is low, and there are difficulties, including the formation of an insoluble film at the anode. Under some circumstances, electrolysis of antimony chloride gives rise to explosive antimony.

However, the only electrolysis that gives better results involves antimony trifluoride. The crude metal can be refined in a sulfate-fluoride solution. Even if the percentage of lead is quite high, lead-free antimony is obtained at the cathode. The excess sulfuric acid in the electrolyte precipitates the lead as lead sulfate, which passes into the anode mud. The energy consumed is 320 kWh/t. Arsenic must be removed beforehand; otherwise, it also deposits on the cathode. Operational details are given in [25].

It is claimed [4, pp. 46, 47; 35] that antimony of 99.2% purity is produced if 96.5% antimony with lead as the main impurity is treated with chloride at 1100 °C. If antimony rich in lead is fused with a sulfur flux, the lead,

as well as zinc, copper, and bismuth, is removed almost completely [4, p. 48]. This method is simpler and cheaper than electrolysis.

Electrolytic refining in molten sodium and potassium chloride at 750–800 °C is said to yield pure antimony. Iron can be reduced rapidly to a residual 50–90 ppm. Lead and copper are difficult to remove; therefore, the antimony should be purified pyrometallurgically beforehand.

14.8 Fine Purification

The antimony used as a solvent for extremely pure silicon must also be extremely pure. Silver, aluminum, chromium, copper, iron, magnesium, manganese, and nickel can be removed almost completely by subliming commercial antimony (99.5–99.9% Sb). However, almost all of the arsenic, lead, tin, and sulfur enters the sublimate, and the product is often contaminated with carbon and silicon. If commercial antimony is alloyed with 0.5–4% manganese, the sublimate is free from tin and largely free from sulfur. If 2% aluminum is used in addition to the manganese, the lead and arsenic contents are also reduced substantially. However, this procedure is not effective unless the rate of sublimation is reduced, to one third in the first case or one tenth in the second. This refining by sublimation is shown schematically in Figure 14.5.

There is growing demand for extremely pure antimony. It is derived from previously purified metal or from antimony(III) oxide. (Table 14.2 shows typical compositions of the starting materials.) The impurities remaining are removed by physical, chemical, and metallurgical methods, including distillation [37], ion exchange [38], liquid–liquid extraction [39], precipitation of intermetallic compounds [9], and zone melting [40–46].

A method described by M. TANENBAUM involves dissolving antimony of 99.8% purity in hydrochloric acid, repeatedly distilling the antimony trichloride obtained to remove the arsenic, and reducing the purified antimony

trichloride with iron pentacarbonyl. Zone melting then gives a product of 99.999% purity [45].

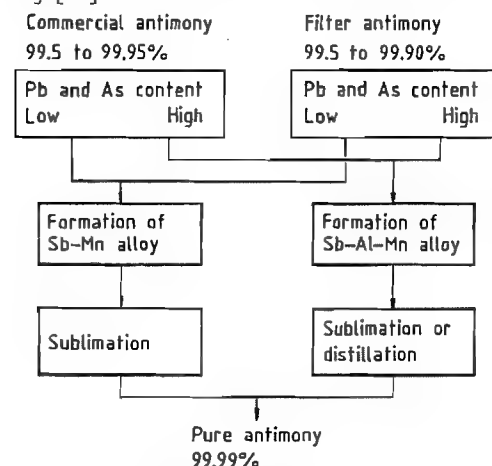


Figure 14.5: Sublimation refining.

Table 14.2: Spectrographic analysis of antimony regulus and of the antimony trioxide obtained by oxidation [36].

Element	Contents, ppm unless otherwise indicated	
	Antimony regulus	Antimony trioxide
As	210	192
Pb	3600	380
Fe	206	158
Ni	85	15
Cu	90	10
Sn	22	12
Bi	17	7
Ag	12	< 1
S	230	106
Sb	99.5%	> 83.38%
Sb as Sb ₂ O ₃	—	> 99.8%

A process patented by M. WILHELM uses hydrogen to reduce antimony pentachloride that has been purified by repeated distillation at 700–900 °C in an atmosphere of argon. The yield is ≤ 70% [46].

Antimony can be separated from numerous impurities by fractional distillation of the anhydrous trichloride or pentachloride [37]. Platinum, gold, silver, manganese, nickel, cobalt, and copper remain behind in the residue. If the heating is carried out carefully, the lead, bismuth, zinc, thallium, and cadmium also remain in the residue. Aluminum chloride, arsenic trichloride, and tin(IV) chloride pass completely into the first fractions, whereas

tin(II) chloride remains behind. Currently only hydrochloric acid solutions are distilled. Under these circumstances, arsenic trichloride distills at temperatures below 110 °C. Because distillation above 110 °C results in considerable loss of antimony, the temperature must be kept slightly under 110 °C.

LEVA and VIGDOROVICH stressed the effectiveness of chemical methods in separating arsenic from antimony and in lowering antimony's heavy metal content. Antimony trichloride is prepared by dissolving technical-grade antimony in hydrochloric acid and is hydrolyzed to give antimony trioxide, which is reduced with pure sucrose. The metal is then purified by zone melting to give a product with 99.995% antimony in 51–53% yield [47].

One rather complex procedure consists of the following: (1) dissolving technical-grade antimony in hydrochloric acid, (2) purifying the antimony trichloride obtained by fractional distillation, (3) converting the purified antimony trichloride into antimony trisulfide, (4) dissolving the sulfide in pure hydrochloric acid, (5) distilling the antimony trichloride, (6) hydrolyzing the trichloride into antimony trioxide, and (7) reducing the oxide with hydrogen. The purity of the antimony exceeds 99.998%, but the yield is low because of the large number of operations.

Very pure antimony trichloride can be purified further by hydrolysis to antimony trioxide with extremely pure water. The trioxide is reduced with purified hydrogen, first at about 600 °C and then at a somewhat higher temperature [9].

The recrystallization of chloroantimonic acid (H₂SbCl₆) efficiently removes final traces of iron [37].

Ion exchange removes cobalt, nickel, zinc, and lead [48, 49]. However, hydrolysis can result in less than quantitative elution.

Liquid-liquid extraction offers a means for refining antimony [39], e.g., by purifying acidic solutions of antimony with alkylphosphoric acid or separating copper, iron, and lead from hydrochloric acid solutions by extraction with ethyl acetate. Pentavalent anti-

mony dissolved in hydrochloric acid can be extracted by dibutyl ether, amyl alcohol, hexyl alcohol, *n*-octyl alcohol, and diisoamyl ether. However, liquid-liquid extraction is seldom used in practice.

The effectiveness of zone melting, usually the last stage in fine purification, depends on the impurities present. Arsenic, tin, and bismuth have unfavorable distribution coefficients (Table 14.3) and are difficult to remove by zone melting. Arsenic must be removed completely in the preceding purification steps. Lead and germanium are easier to remove. In one case, seven passages of the melted zone dropped the nickel, lead, silver, and copper contents to one tenth their original values [44, 45]. The impurity levels, in ppm, are reduced to < 0.5 Ag, < 5 As, < 1 Bi, 0.5 Cu, < 1 Fe, < 5 Ni, 2 Pb, and < 2Sn [36].

Very pure antimony is produced in three grades: > 99.99% (four 9s), > 99.999% (five 9s), and > 99.9999% (six 9s).

Table 14.3: Distribution coefficients in antimony [36].

As	0.64	Pb	0.06
Sn	0.3	Ge	< 0.06
Bi	0.2		

14.9 Alloys and Intermetallic Compounds

Antimony is a component of many lead and tin alloys. These alloys are important materials for making bearings and solders.

The intermetallic compounds AlSb, GaSb, and InSb are important. Zinc antimonide, ZnSb, has interesting semiconductor and thermoelectric properties; cadmium antimonide, CdSb, has interesting semiconductor properties. Antimony is used to dope very pure germanium, silicon, and gallium arsenide to produce *n*-type semiconductors.

14.10 Compounds

Antimony can be trivalent or pentavalent in compounds. Both exist in antimony(IV) oxide, Sb₂O₄, and presumably in the deep violet haloantimonates(IV), such as Cs₂(SbCl₆). The

pentavalent compounds, as well as most of the trivalent ones, are hydrolyzed by water to form antimony salts, e.g., SbOCl, and hydrated oxides. The only halides of antimony that have any industrial significance are the chlorides and fluorides.

Mixed antimony(V) chloride fluorides and bromide fluorides exist, but antimony pentabromide does not. The tribromide, SbBr₃, is chemically similar to the trichloride. Stable complex halides are known, mainly hexahaloantimony anions of the types [SbX₆]³⁻ and [SbX₆]⁻.

14.10.1 Antimony Chlorides

Antimony trichloride (antimony chloride, butter of antimony, caustic antimony), SbCl₃, *mp* 73 °C, *bp* 223 °C, *p* 3.064 g/cm³ at 26 °C, is soft, crystalline, colorless, and very hygroscopic. It is soluble in the usual organic solvents, including benzene, carbon disulfide, carbon tetrachloride, acetone, and ethanol. Only highly concentrated aqueous solutions are stable. Dilution causes antimony(III) chloride oxide, SbOCl, to precipitate. The addition of more water causes further hydrolysis to take place, forming hydrated antimony(III) oxide. Antimony trichloride forms complexes with numerous compounds, some having a striking deep color.

Antimony trichloride is an intermediate in the production of other antimony compounds, a catalyst in organic chlorination and polymerization reactions, and a vitamin A reagent. Large quantities are consumed in rendering textiles, plastics, and other combustible substances flame retardant or self-extinguishing.

Although manufacture from antimony metal and chlorine is expensive, it is feasible on a small scale. The best procedure is to react chlorine with antimony metal in liquid antimony trichloride or concentrated hydrochloric acid. In the first case the temperature can be as high as 200 °C. Equally good results are obtained by dissolving antimony oxides in hot, concentrated hydrochloric acid. Distillation of the crude product or its solution in strong hydrochloric acid in the presence of some me-

tallic antimony or iron (to reduce antimony(V) and iron(III) compounds) then yields pure antimony trichloride.

Stibnite is usually digested in concentrated hydrochloric acid. The antimony passes into solution, whereas the arsenic largely remains in the residue. Disadvantages are the noxious hydrogen sulfide given off and difficulties in heating the strongly acidic solutions.

Antimony chloride oxide (oxychloride), SbOCl , is a white crystalline powder. It is precipitated by hydrolysis when concentrated solutions of antimony trichloride in water or hydrochloric acid are diluted. Because other chloride oxides, e.g., $\text{Sb}_4\text{O}_5\text{Cl}_2$, also form, reaction conditions must be controlled carefully. Antimony chloride oxide is an intermediate in the production of antimony salts and is used in smoke-producing agents.

Antimony pentachloride, SbCl_5 , *mp* 4 °C, *bp* 140 °C, ρ 2.34 g/cm³ at 20 °C, is a pale yellow fuming liquid of unpleasant odor. It can be produced by saturating molten antimony trichloride with chlorine, followed by vacuum distillation. Other methods are the direct chlorination of antimony and the chlorination of antimony oxides or sulfides.

Antimony pentachloride, which easily dissociates and tends to chelate, acts as a chlorine donor in the chlorination of organic compounds. It is also used as a polymerization catalyst.

14.10.2 Antimony Fluorides

Antimony trifluoride, SbF_3 , *mp* 292 °C, *bp* 319 °C, ρ 4.39 g/cm³, is a colorless compound that crystallizes readily and volatilizes at room temperature. If it is exposed to atmospheric moisture, hydrogen fluoride is given off. In organic solvents it is less soluble than the chloride, but both dilute and concentrated aqueous solutions are stable. Antimony trifluoride forms complexes with inorganic compounds. It is an important fluorinating agent, replacing chlorine or bromine by fluorine in both inorganic and organic compounds. It is especially useful for converting acid chlorides to the fluorides. However, if the halogen group in or-

ganic compounds is not very reactive, fluorination is quite sluggish. The rate of reaction can be increased considerably by adding some antimony pentachloride or bromine, in order to form antimony(V) bromide fluorides. Antimony trifluoride is used in the production of pottery and porcelain, and potassium fluoroantimonate(III) is a mordant in dyeing.

Antimony pentafluoride, SbF_5 , ρ 2.99 g/cm³, is a colorless oily liquid at room temperature. Under atmospheric pressure at 7 °C it solidifies to a crystalline mass; it boils at 150 °C. The solid dissolves in water with a violent reaction. The pentafluoride carbonizes and fluorinates organic substances. The chlorine in chlorinated hydrocarbons is replaced by fluorine. Many inorganic substances form complexes with antimony pentafluoride.

Antimony pentafluoride is prepared by treating antimony pentachloride with excess anhydrous hydrogen fluoride. The antimony pentafluoride is separated from the volatile by-products by fractional distillation. It can also be prepared by allowing fluorine to react with antimony powder or molten antimony trifluoride.

The main use of antimony pentafluoride is as a fluorinating agent.

14.10.3 Antimony Tribromide

Antimony tribromide, SbBr_3 , *mp* 96.6 °C, *bp* 280 °C, ρ 4.15 g/cm³, is a white solid. It is used as a mordant.

14.10.4 Antimony Triiodide

Antimony triiodide, SbI_3 , *mp* 167 °C, *bp* 401 °C, ρ 4.78 g/cm³, is a red solid that hydrolyzes readily and forms complex ions. It adds to ethers, aldehydes, and thiols. Antimony triiodide is prepared by reacting iodine with antimony or antimony sulfide in an organic solvent. The triiodide is used in medicine.

14.10.5 Antimony Oxides

Antimony trioxide, Sb_2O_3 , has two modifications: senarmonite below 570 °C, ρ 5.25 g/cm³, and valentinite (white antimony, anti-

mony bloom) above 570 °C, ρ 5.7 g/cm³. The melting point is 656 °C. The commercial product is a white crystalline powder with a density of 5.2–5.8 g/cm³. On heating, it becomes yellow but turns white again on cooling. Antimony trioxide dissolves in acids and alkalis.

Antimony trioxide can be produced by roasting antimony trisulfide, by burning antimony in air or oxygen, by alkaline hydrolysis of antimony halides (trichloride, tribromide, or triiodide), and by hydrolysis of antimony trisulfide with superheated steam. The production of antimony trioxide from antimony trisulfide during ore processing is described in Section 14.6.1.

Antimony tetraoxide, Sb_2O_4 , is a white nonvolatile powder that is soluble in alkalis but not in acids. Its density can differ considerably according to the duration of heating during preparation: 4.07–7.5 g/cm³. Cervantite has a density of 4.07 g/cm³. Antimony tetraoxide is obtained by roasting antimony trisulfide in a current of air or by heating antimony trioxide at 300–400 °C in air. The tetraoxide is used in ceramics.

Antimony pentoxide, Sb_2O_5 , is a whitish yellow powder. On heating, it first turns deep yellow; above 300 °C it turns from brownish yellow to brown but becomes paler above 380 °C. Its density ranges from 3.78 to 7.86 g/cm³. Antimony pentoxide is sparingly soluble in water but readily soluble in alkalis.

The pentoxide can be produced by the action of strong oxidizing agents on mechanized antimony or antimony trioxide. Hydrated antimony pentoxide can be produced by the hydrolysis of antimony pentachloride. The hydrate can be dried without difficulty.

14.10.6 Antimonic Acid and Antimonates

Many years ago antimonic acid was thought to have ortho, pyro, and meta forms, but these have all turned out to be only hydrated antimony oxide, primarily colloidal and differing in water content and solubility in acids and bases.

Potassium antimonate, $\text{K}[\text{Sb}(\text{OH})_6]$. Heating antimony pentoxide with excess potassium hydroxide produces rubbery, granular, or crystalline products. If the substance is recrystallized from a little water, deliquescent mammilated crystals form. Treated with copious cold water or boiled together with a small quantity of water, they are converted into potassium hexahydroxyantimonate, $\text{K}[\text{Sb}(\text{OH})_6]$, which is sparingly soluble in cold water but somewhat more soluble in warm water. Solutions precipitate sodium as the sparingly soluble sodium hexahydroxyantimonate, $\text{Na}[\text{Sb}(\text{OH})_6]$. This reaction is used for the detection of sodium.

Sodium hexahydroxyantimonate was formerly thought to be sodium pyroantimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$. The hexahydroxyantimonate is prepared by melting antimony or antimony oxides with excess sodium nitrate. It is used as an opacifier for glass and enamel.

According to X-ray diffraction analysis, the hydrated antimonates(V) of magnesium, cobalt, and nickel are hexahydroxyantimonates, $[\text{M}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2$, $\text{M} = \text{Mg}, \text{Co}, \text{or Ni}$.

14.10.7 Antimony Sulfides

Antimony trisulfide (stibnite). Sb_2S_3 , *mp* 550 °C, ρ 4.64 g/cm³, has a black crystalline modification and an unstable red-orange modification. If both occur together, the mixture can be carmine or brownish red.

Antimony trisulfide is soluble in alkalis and in concentrated, but not dilute, hydrochloric acid. It also goes into solution if it is boiled in alkali carbonate solutions. However, it precipitates as a reddish-brown powder, of non-definite oxygen content (kermesite), when the solution is cooled. It forms thioantimonates if it is dissolved in alkali-metal sulfides. Antimony trisulfide is a starting material for the production of antimony and antimony compounds.

Antimony pentasulfide, Sb_2S_5 , is an orange to dark red powder. It is doubtful whether stoichiometric Sb_2S_5 exists, because the preparations contain free sulfur and have variable composition. Antimony pentasulfide is insoluble.

ble in water but soluble in alkalis and alkali-metal carbonates. Thioantimonates are formed if the pentasulfide is dissolved in alkali sulfides; the most important of these is Schlippe's salt, sodium tetrathioantimonate, $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$, which is produced on a commercial scale by melting stibnite, sodium sulfide, and sulfur together. Antimony pentasulfide can be obtained from Schlippe's salt by reaction with hydrochloric acid.

14.10.8 Antimony Sulfate

Antimony sulfate, $\text{Sb}_2(\text{SO}_4)_3$, ρ 3.62 g/cm³, is a hygroscopic compound in the form of needles with a silken sheen. When antimony or antimony trioxide, trisulfide, or oxychloride is dissolved in hot sulfuric acid, antimony sulfate or antimony salts are recovered. Antimony sulfate is used in the manufacture of explosives and in fireworks.

14.10.9 Stibine

Stibine, antimony hydride, SbH_3 , is a poisonous, foul-smelling gas of density 5.685 g/L (STP). The liquid boils at -88.5 °C. The gas is slightly soluble in water, soluble in alcohol, and very soluble in CS_2 . Its formation is endothermic, $\Delta H_f = 140$ kJ/mol, and it easily decomposes to hydrogen gas and antimony metal. Stibine is used to prepare *n*-type silicon semiconductors.

14.11 Chemical Analysis

The presence of antimony can be demonstrated by the Marsh test. There are a number of classical gravimetric and volumetric methods for determining antimony. A popular colorimetric method is based on a complex between rhodamine B and antimony. Instrumental methods for traces of antimony include polarography, emission spectrography, neutron activation, and atomic absorption [50].

14.12 Uses

Antimony metal is used mainly in alloys with lead or other metals. Nearly 50% of the total demand is accounted for by storage batteries, power transmission devices, communications equipment, type metal, solder, and ammunition. The compounds of antimony have a wide range of industrial uses, including uses in flame retardants, industrial chemicals, rubber, plastics, ceramics, and glass. The uses of antimony alloys, oxides, and sulfides are given in this section, whereas the special uses of the less important compounds are described with the compounds themselves in Section 14.10.

Secondary antimony is consumed chiefly as antimonial lead. These antimony-lead alloys find use in battery grids, pumps and pipes for chemicals, tank linings, roofing, and cable sheaths. The antimony increases their strength and inhibits chemical corrosion. Hard tin-antimony crystals lengthen the life of anti-friction bearings. Antimony increases hardness, minimizes shrinkage, gives sharp definition, and lowers the melting point of type metal. Precision in duplication, durability, the metallic luster, and economy are characteristics of antimonial alloys such as pewter. The amount of antimony used to harden the lead alloys for car battery grids has been reduced over the years. Antimony has been replaced by other metals in batteries for starting, lighting, and ignition, although it is still used in some replacement batteries.

High-purity antimony metal is being used in increasing amounts in intermetallic compounds for electronic semiconductors and thermoelectric devices.

The decline in the use for batteries is being offset by increased consumption of *antimony oxide* as a flame retardant, now the dominant market for primary antimony. In fact at present the main use for antimony(III) oxide is as a flame retardant in plastics. Large quantities of both antimony trioxide and trichloride are consumed in rendering textiles, plastics, and other combustible substances flame retardant or self-extinguishing. Textile finishes consist-

ing of antimony trioxide, chlorinated paraffin wax, and lime protect the fibers from damage by ultraviolet radiation. Further, antimony trioxide is used extensively in plastics, metalware, and ceramic enamels. It is used as a white pigment in paints. Its unusual light-transmission characteristics make it useful in glass manufacture.

The crude commercial *antimony sulfide* can be used directly in the manufacture of matches or Bengal lights. For the production of high-quality pyrotechnics, e.g., electrically ignited detonators, the crude antimony must be remelted in a reducing atmosphere at as low a temperature as possible. Under these circumstances, a well-crystallized, readily ground product is obtained. For several years, synthetic antimony(III) sulfide that satisfies the severe requirements imposed in pyrotechnics has been prepared from sulfur and antimony.

Antimony compounds yield black, vermilion, yellow, and orange pigments. Antimony trisulfide, which reflects infrared radiation much like vegetation, is a constituent of camouflage paints. Antimony pentasulfide is used as a vulcanizing agent in rubber.

Antimony finds a number of uses in ammunition. In alloys it hardens lead small-arms bullets and shot. Tracer bullets have a basal recess containing a light-emitting antimony sulfide mixture. A small annual tonnage of antimony trisulfide goes into the production of percussion primers, in which it acts as a friction composition and heat-transfer medium.

Burning antimony trisulfide emits a dense white smoke, which is used in visual fire control, marine markers, and visual signaling.

14.13 Economic Aspects

Antimony is produced from its ores and as a smelter by-product in about 20 countries, on all continents. Most of the 1979 production is attributed to Bolivia, South Africa, China, and the former Soviet Union, which together contributed 67 of the estimated total (also see Section 14.4). Table 14.4 shows the mine and smelter production by country in 1978.

The total 1978 world production of primary and secondary antimony was approximately 145 600 short tons; therefore, 50% is produced from scrap.

The U.S. consumption by end use is shown in Table 14.5.

Table 14.4: World production of primary antimony in 1978, tons of metal.

Country	Mine	Smelter
North America		
United States	1 213	12 800
Others	5 780	1 270
Total	6 993	14 070
South America		
Bolivia	12 671	2 903
Others	1 148	453
Total	13 819	3 356
Europe		
Belgium	—	7 711
France	—	7 983
Germany	—	2 268
Former USSR	7 892	6 350
Yugoslavia	2 758	544
Others	2 210	5 217
Total	12 860	30 073
Africa		
South Africa	9 093	—
Others	2 465	—
Total	11 558	—
Asia and Australia		
Japan	—	7 257
China	12 700	10 433
Thailand	2 873	272
Other Asian countries	3 597	453
Australia	1 514	—
Total	20 684	18 415
World total	65 914	65 914

Table 14.5: U.S. antimony consumption, tons.

	1970	1974	1979 ¹
Transportation, including batteries	18757	17782	18506
Flame retardants	2358	6063	8890
Chemicals	5652	6871	5806
Miscellaneous	2377	1077	3068
Rubber products	2540	3638	2721
Machinery	1451	2020	2268
Ceramics and glass	1633	2425	2086

14.14 Toxicology

Antimony, which is considered a nonessential element, is comparable in its toxicological

behavior to arsenic and bismuth [51]. In analogy to arsenic, trivalent antimony compounds generally are more toxic than the pentavalent compounds [52]. Poisoning with antimony and its compounds can result from acute and chronic exposure, especially from exposure to airborne particles in the workplace; to a minor extent, exposure occurs through treatment of tropical diseases with antimony compounds.

Most antimony compounds, mainly those with poor water solubility, are absorbed only slowly from the gastrointestinal tract. Trivalent compounds especially tend to accumulate in the human body, because they are excreted very slowly via urine and feces [52]. Antimony and its compounds react readily with mercapto groups in various cellular constituents, especially in enzymes, blocking their activity. After acute and chronic exposure highest concentrations are found in liver, kidney, adrenals, and thyroid.

Acute Toxicity. Acute oral poisoning by antimony compounds after ingestion of contaminated drinks was observed in 150 children; the symptoms were nausea, diarrhea, and vomiting [53]. Acute respiratory exposure of seven workers to 70–80 mg/m³ of antimony trichloride, SbCl₃, resulted in irritation of the upper respiratory tract [54]. Antimony pentachloride, SbCl₅, caused severe pulmonary edema in three cases, two of them being lethal [55]. Stibine, SbH₃, a highly toxic, relatively unstable gas with an unpleasant odor, causes symptoms of the central nervous and circulatory systems, such as nausea, vomiting, headache, slow breathing, weak pulse, hemolysis, hematuria, abdominal pain, and death [56, 57]. Stibine is generated if nascent hydrogen can react with antimony in acid, e.g., in lead acid batteries, where antimony may be a component of the battery plates [58].

People who are exposed to antimony and its compounds often show transient pustular skin eruption [59]. These "antimony spots" mainly occur in those regions of the skin that are exposed to heat and sweat.

Antimony trifluoride and pentafluoride are highly toxic and irritant to the skin; they cause

eczematous eruptions and inflammation of mucous membranes of nose and throat.

Chronic Toxicity. Chronic poisoning after oral ingestion of antimony compounds has been observed in many cases of clinical treatment with antimony compounds. These chronic intoxications resulted in nausea and vomiting [60]; liver damage, with increased plasma values of aspartate-aminotransferase and alanine-aminotransferase [61]; changes in the electrocardiogram, indicating a cardiotoxic effect of these compounds [62]; and even sudden death [63].

Most cases of chronic respiratory intoxications result from exposure to airborne particles in the workplace. In a study involving 78 workers in antimony smelters, symptoms such as soreness, nosebleeds, rhinitis, pharyngitis, pneumonitis, and tracheitis could be observed after exposure times of up to five months, the air containing antimony trioxide, Sb₂O₃, in a concentration of 4.7–11.8 mg/m³ [59]. Long-term exposures often result in lung X-rays that are similar to those seen in pneumoconiosis [64]. Workers who had been exposed to Sb₂O₃ for up to 28 years had pneumoconiosis (21%) and symptoms of emphysema (42%) [65]. Brieger et al. [66] extensively examined 125 workers who had inhaled antimony trisulfide, Sb₂S₃, in air at concentrations of 0.6–5.5 mg/m³ for 8–24 months. An increased morbidity and mortality were observed among these workers. Changes in the electrocardiogram were seen in 37 cases out of 75. In addition, a significantly higher incidence (6%) of peptic ulcers occurred within the group of workers exposed to antimony compared to the incidence within the total plant population (1.5%). During the period of this study, six workmen died suddenly, and two others died from chronic heart diseases. After extensive exposure to antimony fumes, workers showed gastrointestinal symptoms, such as diarrhea, vomiting, and abdominal convulsions [59].

Mutagenicity, Carcinogenicity. Antimony has been demonstrated to be mutagenic in bacteria and phages, and to induce chromosomal aberrations and abnormal cell divisions in ani-

mal and plant cells [67]. Antimony trioxide is a suspected carcinogen in humans [68].

Toxicological Data. Antimony, Sb, MAK 0.5 mg/m³, LDLo 100 mg/kg (rat, intraperit.) [69].

Antimony hydride, stibine, SbH₃, MAK 0.1 ppm (0.5 mg/m³), LCLo 92 ppm (guinea pig, inhalation, 1 h) [70].

Antimony trifluoride, SbF₃, MAK 0.5 mg/m³ (as Sb), TLV 0.5 mg/m³ (as Sb), LDLo 100 mg/kg (guinea pig, oral) [71].

Antimony pentafluoride, SbF₅, MAK 0.5 mg/m³ (as Sb).

Antimony trichloride, SbCl₃, MAK 0.5 mg/m³ (as Sb), TLV 0.5 mg/m³ (as Sb), TDLo 73 mg/m³ (human, inhalation) [54].

Antimony pentachloride, SbCl₅, MAK 0.5 mg/m³ (as Sb), TLV 0.5 mg/m³ (as Sb), LD₅₀ 1115 mg/kg (rat, oral) [72], causes mutation in *Bacillus subtilis* at 30 µL/disk [73].

Antimony trioxide, Sb₂O₃, carcinogenic potential suspected for humans, TLV 0.5 mg/m³ (as Sb), TCLo 4.2 mg/m³ during 52 weeks, carcinogenic (rat, inhalation) [74].

Antimony pentoxide, Sb₂O₅, LDLo 4000 mg/kg (rat, intraperit.) [69].

Antimony trisulfide, Sb₂S₃, TLV 0.5 mg/m³ (as Sb), TCLo 580 µg/m³ during 35 weeks (humans, inhalation) [66], LDLo 1000 mg/kg (rat, intraperit.) [69].

Antimony pentasulfide, Sb₂S₅, TLV 0.5 mg/m³ (as Sb), LD₅₀ 1500 mg/kg (rat, intraperit.) [69].

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15 Bismuth

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15.1 Introduction

Bismuth belongs to the fifth main group of the periodic table. Its chemical behavior is similar to that of the other group VB elements arsenic and antimony.

The electron configuration is $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$. Only one stable isotope, ^{209}Bi , is known, but there are several unstable isotopes (^{199}Bi – ^{215}Bi). Isotopes with mass number > 210 are found in the natural decay chains of radioactive elements. Isotopes with mass number < 208 have been formed in nuclear transformations.

Bismuth is used as an alloying component in fusible alloys, but no commercial use of pure bismuth metal is known. Consumption seems to be declining; the current world production is only about 4000 t/a.

15.2 History

The name of the metalloid is to be found in all western languages. It is probably of Ger-

manic origin and was mentioned first by ALBERTUS MAGNUS (1193–1250). Around 1450 BASILIUS VALENTINUS calls it *bismutum* and PARACELSUS (1493–1541) named the metal *wismut*. GEORGIUS AGRICOLA thought it to be a special kind of lead and describes the winning of *plumbum cinerum*. In 1739, PORT finally distinguished pure bismuth from other metals. Bismuth was known as a low-melting alloying element in the 16th and 17th centuries, and it was also used in the form of the subnitrate – in cosmetics and medicine. Industrial production began around 1830 in Saxony and increased after the first bismuth ores were shipped to Europe in 1867. The discovery of fusible alloys caused production to increase in the 1930s [1–4].

15.3 Properties [1–6]

Physical Properties. Bismuth is a heavy, lustrous, silver-white metal with a slight pink cast. If solidification is slow, large brittle crystals form. For a metal, bismuth has some unusual properties:

- Like germanium and gallium, its volume increases on solidification. The increase is 3.32%.
- Bismuth is the most diamagnetic metal. Its specific susceptibility is $-16 \times 10^{-9} \text{ m}^3/\text{kg}$ at 293 K.
- Only liquid mercury has a lower thermal conductivity.
- The electrical resistance of solid bismuth is greater than that of liquid bismuth. Superconductivity has not been detected. The increase in resistivity in a magnetic field (the Hall effect) is the largest of all metals.
- Bismuth alloys show large thermoelectric effects.
- With the exception of beryllium, bismuth has the lowest absorption cross section for thermal neutrons.

Atomic radius	0.18 nm
Melting point	271.40 °C
Boiling point	1564 °C
Crystal system	rhombohedral
Lattice constant	$a = 0.47457 \text{ nm}$ $\alpha = 57.24^\circ$
Latent heat of fusion	11 280 J/mol
Latent heat of vaporization	178 632 J/mol
Volume expansion on solidification	3.32%
Coefficient of linear expansion	$13.5 \times 10^{-6} \text{ K}^{-1}$
Density at 20 °C	9790 kg/m ³
Electrical resistivity	
at 0 °C	106.8 $\mu\Omega\text{cm}$
at 1000 °C	160.2
Specific heat at 25 °C	25.5 Jmol ⁻¹ K ⁻¹
Thermal conductivity	
at 0 °C	8.2 Js ⁻¹ m ⁻¹ K ⁻¹
at 300 °C	11.3
at 400 °C	12.3
Vapor pressure	
at 893 °C	$1.013 \times 10^{-3} \text{ bar}$
at 1053 °C	1.013×10^{-2}
at 1266 °C	1.013×10^{-1}
Surface tension	
at 300 °C	376 mN/m
at 400 °C	370
at 500 °C	363
Absorption cross section for thermal neutrons	$(3.4 \pm 0.2) \times 10^{-30} \text{ m}^2/\text{atom}$
Hardness, Brinell	184 N/mm ²
Hardness, Mohs	2.5
Poisson's ratio	0.33
Shear modulus	12 400 MPa
Modulus of elasticity	338 GPa
Tensile strength at 20 °C	
soft	5 MPa
hard	20
Diffusion coefficient of Bi in dilute Bi-Sn alloys [7]	$(2.33 \pm 0.18 \text{ cm}^2/\text{s}) \times$

Viscosity [8]

at 300 °C	1.65 MPa·s
at 350 °C	1.49
at 400 °C	1.37
at 500 °C	1.19
at 600 °C	1.06
Hall coefficient at 18 °C	$-6.33 \times 10^{-7} \text{ m}^3\text{A}^{-1}\text{s}^{-1}$
Magnetic induction	0.393 T

Thermal expansion, compressibility, heat conduction, self-diffusion, electrical resistivity, and mass susceptibility depend on crystal orientation [8].

Chemical Properties. Bismuth is not very reactive; generally, it is less reactive than lead and more reactive than silver. It shows annealing colors when heated but otherwise does not oxidize in dry air. Liquid bismuth is covered by an oxide film of Bi_2O_3 that protects it from further oxidation. At 817–821 °C the oxide melts, and then the metal oxidizes rapidly. Therefore it is possible to separate bismuth from the noble metals by cupellation. Moisture is slightly oxidizing at high temperatures. Other possible oxides are Bi_2O_4 and Bi_2O_5 . In most compounds, bismuth has a 3+ oxidation state, although in some compounds, such as Bi_2O_5 , bismuth pentahalides, and a number of organobismuth compounds, it has oxidation state 5+. Stable compounds with selenium and tellurium have interesting semiconductivity and thermoelectric properties. Bismuth has a standard electrode potential of +0.28 V, placing it between antimony and copper in the electrochemical series. It can be separated from lead by electrolysis [2].

15.4 Occurrence [2, 3]

Bismuth ranks 64th in abundance in the earth's crust; like antimony and cadmium, its abundance is estimated to be 0.17 to 0.2 ppm. Most bismuth sulfides occur associated with lead, copper, and silver. A few deposits in which bismuth is a major mineral are also known. The most important pure bismuth minerals are native bismuth and bismuth glance, Bi_2S_3 . Other bismuth minerals are bis-

$10^{-4} e^{-Q/RT}$ where
 $Q = 10.6719 \pm 0.365$
kJ/mol

mite, Bi_2O_3 ; bismuth ocher, $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; and bismutite and bismutosphaerite, $\text{Bi}_2(\text{O}_2/\text{CO}_3)$.

Deposits from magmatic granite nearly always contain bismuth in low concentration. Bismuth is mainly found surrounding intrusive rocks, thus it is perimagmatic. Together with complex minerals of silver, copper, and lead, it can end up in deposits far from igneous bodies. If the other elements are carried further, the bismuth ocher left may be worth working.

Significant European deposits are situated in Spain and Saxony (Germany). In China bismuth occurs together with tungsten, molybdenum, and tin ores, which may be dressed up to 60–63% Bi. Bismuth minerals are found together with tungsten ores in South Korea. Important ex-USSR deposits are in Adrasman, Tajikistan. The most important bismuth deposits are in South America. The Cu, Pb, and Zn concentrates from Peru (Junin and Oroya) contain bismuth; in Bolivia, bismuth is found together with tin and sometimes with tungsten. Mines are found in Tasua and Chorolque, Department Potosi, and Caracoles, Cimsa Cruz Cordillere, where oxide and sulfide concentrates with 35–45% Bi are produced.

15.5 Production

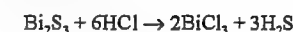
Bismuth is produced in small amounts from so-called bismuth ores or concentrates. The largest amounts are recovered as by-products from lead and copper production, mostly during processing complex copper concentrates. Bismuth is also won from molybdenum, tungsten, and tin concentrates.

15.5.1 Crude Bismuth from Bismuth-Rich Mixed Concentrates

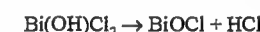
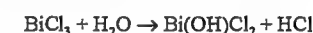
Only in rare cases are as-mined ores rich enough to be treated directly to produce metal. Usually the ores have to be enriched before processing. Because of the large variety of ore compositions there is no standard procedure for upgrading. A special process has to be developed for each deposit: mechanical enrichment and flotation are usually the preferred

methods. Often these methods do not produce the desired results, and the bismuth concentrates must be enriched further, either by leaching or by volatilization, or some combination of both.

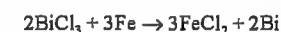
For the selective separation of bismuth from complex nonferrous metal concentrates that contain up to several percent bismuth, leaching with hydrochloric acid has proved effective:



If weak acid is used, the reaction must be supported with H_2O_2 . The bismuth is precipitated by hydrolysis on dilution or partial neutralization,



or by cementation with iron turnings,



Neither procedure leads to a pure precipitate. The hydrolysis precipitates slightly soluble chlorides along with the bismuth compound. These chlorides can be precipitated only partially in advance. The cementation also precipitates the more noble metals. Such precipitates are usually smelted with soda or Na_2S to separate bismuth metal from copper and lead, which go into a matte low in bismuth.

Processing of Complex Molybdenum-Bismuth Preconcentrates. The bismuth in a preconcentrate containing 4.8% Bi, 14.5% Mo, 17.9% Fe, 8.0% Pb, 2.5% Cu, and 7.4% SiO_2 can be dissolved with concentrated hydrochloric acid; molybdenum does not dissolve. The dissolved bismuth is then cemented with iron turnings.

	Composition, %		
	Mo	Bi	Cu
Concentrates before leaching	14.5	4.8	2.5
Concentrates after leaching	16.3	0.02	— ^a
Cementate	<0.1	86–95	<0.1

^a Not usually given.

The enriched product is refined. The bismuth-free molybdenum preconcentrates may

be upgraded further by flotation [9]. The flow diagram of this process is shown in Figure 15.1. The Molybdenite Corporation of Canada floats bismuth-containing molybdenum ores: 70–80% of the Bi and 93–95% of the Mo are recovered. This process produces a highly enriched Mo–Bi concentrate and an Mo concentrate (Table 15.1). In the first stage the Mo–Bi concentrate is leached with hydrochloric acid at 90–100 °C and finally with nitric acid. BiOCl precipitates from the bismuth-containing solution upon dilution to pH 2–3. Silver and lead chlorides also precipitate. Copper may be cemented afterwards with iron scrap. The crude bismuth has to be refined further [10].

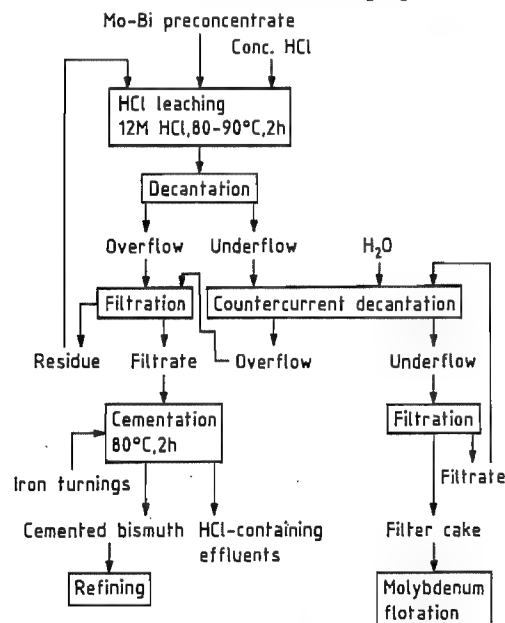


Figure 15.1: Hydrometallurgical separation of bismuth from Mo–Bi preconcentrate [9].

Processing of Sulfidic Copper–Bismuth Concentrates. The recovery of crude bismuth from sulfidic Cu–Bi concentrates is best illustrated by two examples.

The bismuth can be dissolved selectively with HCl in the presence of an oxidizing agent and precipitated as BiOCl by hydrolysis on

neutralization of the solution. Figure 15.2 shows the flow diagram, and Table 15.2 shows the distribution of elements in the intermediate products. The wash water is recycled, which increases the recovery of Cu, Bi, and Pb. Altogether 95% of the bismuth (and ≈ 1% of the copper) is found in the BiOCl precipitate, and 98% of the copper (and ≈ 4% of the bismuth) is found with the copper concentrate and cement copper.

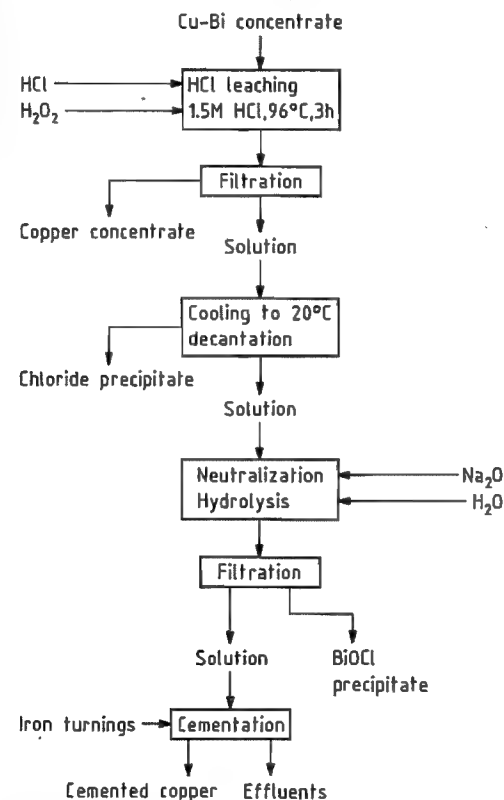


Figure 15.2: Hydrometallurgical separation of Bi from Cu–Bi concentrates [11].

Table 15.1: Bismuth separation from bismuth-containing molybdenum ores [10].

Substance	Concentration, %			
	MoS ₂	Bi	Cu	Fe
Ore, as mined	0.32	0.042	≤ 0.1	0.5–2.0
Mo–Bi concentrate	75–80	6–9	1P2	—
BiOCl	—	75	0.3 Ag	4 Pb
Crude bismuth	—	96	0.3 Ag	3 Pb

Table 15.2: Distribution of elements (%) in various intermediates of the oxidizing leaching process for Cu–Bi concentrates [11].

Substance ^a	Bi	Cu	Pb	Ag	Au
Cu concentrate	4	76	80	82	100
Chloride precipitate	< 1	—	9	8	—
BiOCl	74	< 1	< 2	< 3	—
Cemented copper	—	14	< 1	—	—
Wash water	21	8	3	—	—
Effluents	—	< 1	—	—	—

^aPercentage of the initial concentrations in the Cu–Bi concentrate. These initial concentrations are 1.7% Bi, 10.8% Cu, 8.0% Pb, and 0.34% Ag. Also present are 26.0% Fe, 29.4% S, 12.0% SiO₂, and 2.8% Zn.

Table 15.3: Bismuth contents and distribution during conventional lead smelting [13].

Substance	Bi content, %	Bi distribution, %
Sinter roasting input		
Lead concentrates	0.03	66.3
Lead flue dusts	0.06	13.9
Copper flue dusts	0.07	15.1
Sinter roasting output		
Sinter	0.04	97.5
Flue dust	0.08	2.5
Blast furnace input		
Sinter	0.04	75.0
Drosses	0.07	14.4
Pb–Ag residue	0.02	3.1
Recycled slag	0.08	5.9
Blast furnace output		
Pig lead	0.08	77.3
Flue dust	0.04	12.8
Slag	0.001	1.1

The Cu–B concentrate is leached first with hydrochloric acid (90–100 °C) and then with nitric acid. BiOCl precipitates from the solution after dilution to a pH of 2–3. Silver and lead chlorides coprecipitate. Copper may be cemented afterwards with iron scrap [11].

Bismuth copper concentrates are smelted in Telamayu, Bolivia, under reducing conditions after addition of soda to produce crude bismuth (> 92% Bi), a lean alkaline copper matte (< 10% Cu, < 0.3% Bi, < 20% Na), and a slag waste. The soda makes the slag low melting (< 1000 °C) and keeps the Bi content of the copper matte as low as possible. The flow sheet is shown in Figure 15.3. The crude bismuth is refined by conventional pyrometallurgical methods, the prerefining in Bolivia, the final refining in Belgium [12].

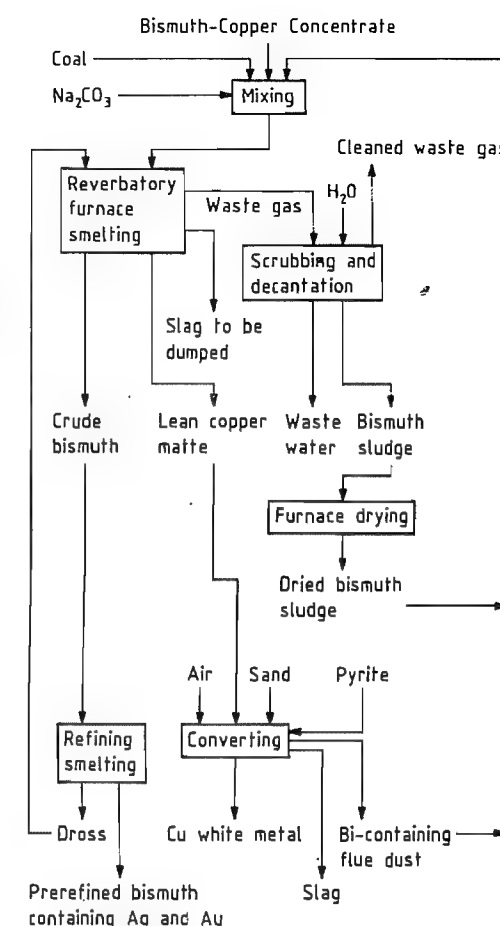


Figure 15.3: Processing of Bi–Cu concentrates in Telamayu, Bolivia [12].

15.5.2 Crude Bismuth from Lead Concentrates

Lead concentrates can contain significant quantities of bismuth. The average bismuth contents (g/t) are given below for several such concentrates [2]:

Kassandra, Greece	1800–2400
La Oroya, Peru	2300
Trepča, Yugoslavia	1600
Saxberget, Sweden	1100–1200
Milpo, Peru	1050
Aouli, Morocco	900
Atacocha, Peru	850
Raura, Peru	300–500
Bathurst, New Brunswick	450

Kimberley, British Columbia	350
Renström, Sweden	350
Garpenberg, Sweden	140–240
Rammelsberg, Germany	130–150

Lead production is usually carried out in two steps: (1) sintering and (2) reduction in a blast furnace. During this process the bismuth follows the lead without major losses, despite the volatility of bismuth (Table 15.3). In any case, the flue dusts are usually recycled. The loss of bismuth in the slag is low, since bismuth is reduced before lead [14].

Usually, bismuth is only a trace element throughout lead processing: only during lead refining is it enriched up to a few percent. The clean separation of bismuth from lead and the other elements present cannot be done by pyrometallurgical or electrolytic refining. Bismuth has less tendency than lead to form oxides, sulfides, or halides. Therefore, normal pyrometallurgical refining is not possible. Also, it is less electropositive:

$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}_{(s)}$	-0.14 V
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}_{(s)}$	-0.13 V
$\text{Sb}^{3+} + 3\text{e}^- \rightarrow \text{Sb}_{(s)}$	+0.2 V
$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}_{(s)}$	+0.28 V
$\text{As}^{3+} + 3\text{e}^- \rightarrow \text{As}_{(s)}$	+0.3 V
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}_{(s)}$	+0.345 V

Electrolytic refining can separate lead and bismuth, but Sb, As, Bi, and Cu remain together.

15.5.2.1 Pyrometallurgical Separation of Bismuth from Metallic Lead

One method has been found to separate bismuth from lead: precipitation of the intermetallic compound CaMg_2Bi_2 . The CaMg_2Bi_2 forms after addition of calcium–magnesium alloy to bismuth-containing lead melt (Kroll–Betterton process). The calcium and magnesium are added at 420 °C to the lead bath. The temperature is allowed to fall at a rate of 20 K/h until it is close to the melting point

(330 °C). Then the intermetallic compounds rich in bismuth solidify, and, having a lower density than lead, float to the top, where they can be removed in the dross by skimming. The simultaneous solubilities of Ca, Bi, and Mg in lead close to its melting point can be calculated from the solubility product [15].

$$[\text{Mg}, \%]_{\text{Pb}}^2 \times [\text{Ca}, \%]_{\text{Pb}} \times [\text{Bi}, \%]_{\text{Pb}}^2 = 4.3 \times 10^{-8}$$

Figure 15.4 shows these equilibrium solubilities of bismuth in the lead corner of the Pb–Ca–Mg system. In practice, the bismuth concentrations in refined lead are slightly higher than the calculated values: usually $\approx 0.01\%$. This is shown in Table 15.4 for two reported cases. The final bismuth concentration can be reduced below 0.01% if antimony is added to a melt already treated with Ca and Mg [18].

The Ca–Mg consumption can be calculated. Because the residual concentrations of Ca and Mg are greater for lower bismuth contents, the specific consumption is much greater for low Bi contents, as can be seen in Table 15.5 [16, 17].

Earlier, a mixture of K and Mg was used to separate the bismuth (Jollivet–Penarroya process), but the process is no longer in use. The reactions are analogous [15].

Table 15.4: Concentrations (%) in molten lead after bismuth separation and calculated solubility product.

Smelter	Bi	Mg	Ca	$[\text{Mg}]_{\text{Pb}}^2 \times [\text{Ca}]_{\text{Pb}} \times [\text{Bi}]_{\text{Pb}}^2$	Ref.
Chimkent	0.009	0.145	0.066	1.1×10^{-7}	[16]
Norddeutsche Affinerie	0.014	0.1	0.03	0.6×10^{-7}	[17]

Table 15.5: Specific Ca and Mg consumptions for Bi removal from lead melts.

[Bi]Pb, %		Specific consumption, kg metal per kg Bi content	
before	after	Ca	Mg
0.05	0.009	1.06	3.5 calculated
0.09	0.009	0.62	2.05 calculated [16]
0.18	0.009	0.36	1.06 calculated [16]
0.2	0.020	0.25	0.60*
0.68	0.014	0.15	0.39 [17]

*Calculated from data in Ullmann, 3rd ed., vol. 18, p. 635.

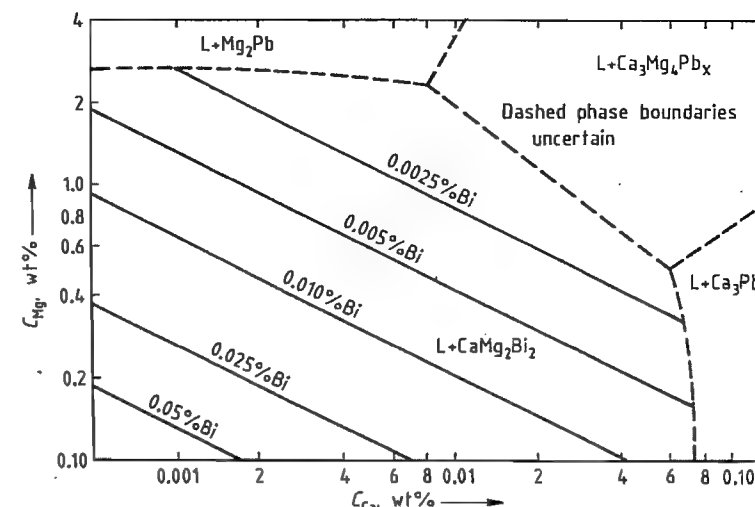


Figure 15.4: The Pb–Bi–Ca–Mg system, the liquidus surface in the lead corner [15].

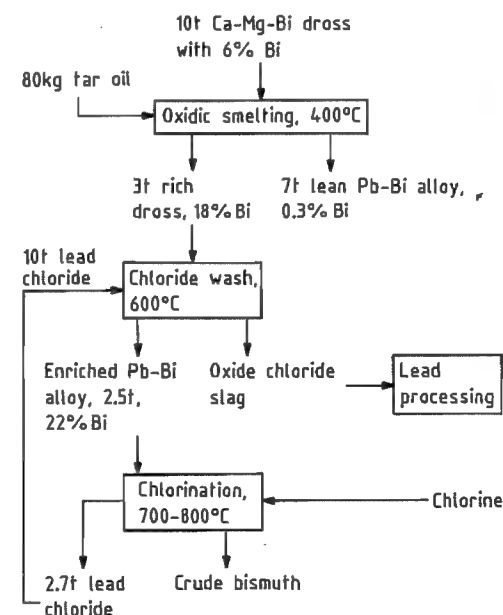


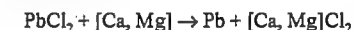
Figure 15.5: Conventional treatment of bismuth dross [19].

15.5.2.2 Processing of Bismuth-Containing Drosses

The dross resulting from the Kroll–Betterton process contains only a few percent bismuth. A typical composition is 6% Bi, 0.8%

Ca, and 1.3% Mg. The rest is Pb. If possible, the dross is enriched before bismuth recovery.

Several methods are available: liquation, pressing with a Howard press, partial oxidation, or partial chlorination. Usually one-stage enrichment is insufficient, so a multistage procedure is chosen. Often tar oil is mixed with the hot dross, which then burns immediately, oxidizing part of the Mg and Ca. At the same time the lead melts and separates from the dross. The flow sheet is shown in Figure 15.5. The solid dross remaining can be smelted to a lead–bismuth alloy. Calcium and magnesium can be removed from the dross by adding lead chloride.



The resulting Pb–Bi alloy containing 20–30% bismuth is chlorinated at 700–800 °C. The lead is converted to PbCl_2 . The crude bismuth contains less than 0.5% lead.

A process proposed by ASARCO (Figure 15.6) minimizes the costs. Vacuum filtration at 450 °C separates most of the lead without oxidation. The filter cake is heated slightly higher and burns, mostly by self-sustaining combustion. Washing with PbCl_2 separates the oxide residue into a Pb–Bi alloy and an oxide chloride slag. The alloy is refined in the usual way [19].

Although chlorine can be used to separate lead and bismuth, chlorine consumption is high and PbCl_2 , not Pb, is produced. Both the Norddeutsche Affinerie, Hamburg, and the Vieille Montagne, Belgium, have chosen another method. The Bi-Cu-Mg dross is soaked in a Pb-Bi melt. The Ca and Mg are oxidized in the presence of small amounts of NaOH, < 20 kg per tonne dross. The bismuth-rich lead is cast into anodes and electrolyzed to pure lead and anode slime, which can be melted to give crude bismuth. Only the lead remaining in the crude bismuth is chlorinated. In this way the largest portion of the lead is obtained directly as metal [17, 20].

15.5.2.3 Electrolytic Separation of Lead and Bismuth. Bismuth Production

Some lead producers use electrolytic lead refining, usually with $\text{PbSiF}_6\text{-H}_2\text{SiF}_6$ electrolyte, which allows an almost complete lead bismuth separation, independent of the bismuth content. Final bismuth contents ≤ 10 ppm can be achieved [17, 19, 21]. Almost all the bismuth goes into the anode slimes, which can contain between 2 and 25% Bi, depending on the bismuth content of the anodes (Trail, 2–4%; Oroya, 18–22%; Kamioka, 22% [2]).

At Centromin (formerly Cerro de Pasco Corp.) in La Oroya, Peru, dried anode slimes (35% Sb, 22% Bi, 14% Pb, 9% Ag, 0.03% Au) are smelted in a reverberatory furnace to partially evaporate the antimony. The metal then is 22.9% Sb, 30.8% Bi, 21% Pb, 19.6% Ag, and 0.069% Au. This metal is air-oxidized in a converter in two stages. In the first stage, at 900–1000 °C, a metal with $\approx 45\%$ Bi is produced. In the second stage, at 1100–1200 °C, a high-grade lead silver-bismuth alloy, 50–55% Ag and 30% Bi, and a slag with 40% Bi, 11% Pb, 4% Cu, and 2.5% Sb are obtained. This slag can be reduced at 1000–1100 °C to crude bismuth (73% Bi, 17% Pb, 3.6% Ag, 3% Cu) [2, 22]. The flow sheet is shown in Figure 15.7.

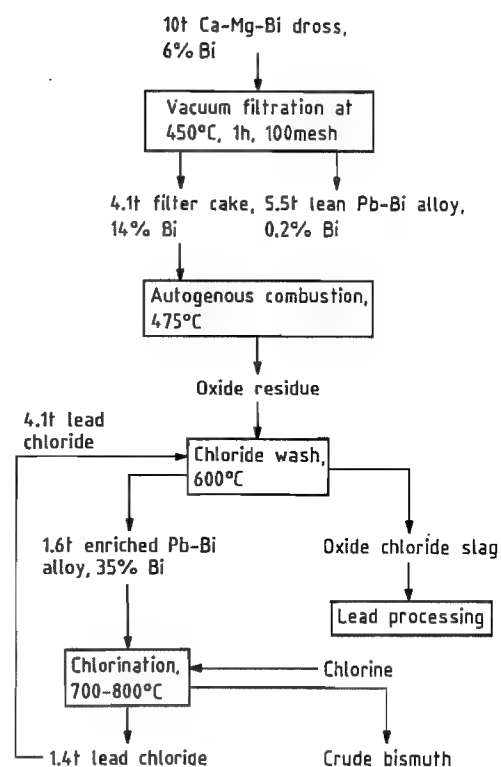


Figure 15.6: Bismuth treatment at ASARCO [19].

The anode slimes of the electrolytic lead refinery of Consolidated Mining and Smelting Corp., Trail, Canada, contain only 2–4% Bi. These anode slimes are smelted in a reverberatory Furnace at 900–950 °C, and the resulting alloy is oxidized in two stages, at 800–850 °C for arsenic and antimony oxidation and at 1000–1100 °C for oxidation of bismuth, lead, and copper. The slag of the second stage is the raw material for bismuth recovery. It is reduced to give a Pb-Bi alloy with 25–30% Bi, which is desilvered and again electrolyzed. The secondary anode slime consists mostly of bismuth. It contains 2% Pb and only traces of other elements. The slime is reduced to crude bismuth. After treatment with chlorine to remove lead, final treatment with caustic soda yields bismuth of 99.994% purity (20 ppm Pb, 14 ppm Cu, 33 ppm Ag). Figure 15.8 shows the flow sheet [2].

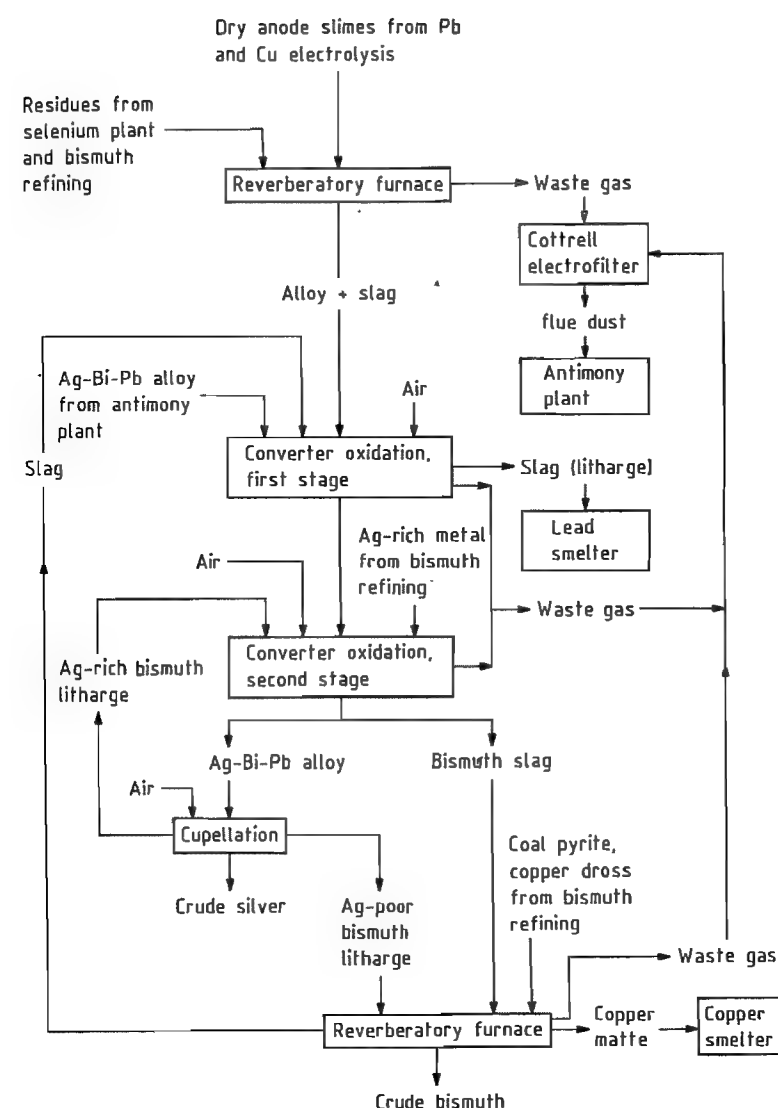


Figure 15.7: Recovery of crude bismuth from anode slimes at La Oroya, Peru [23].

The lead anode slime in San Gavino Monreale is treated to produce antimonial lead and bismuth.

Norddeutsche Affinerie has a special status among bismuth producers. The Kroll-Betterton procedure gives a Bi-Ca-Mg dross, which is separated from lead (0.05–3.5% Bi) and melted to a Pb-Bi alloy. This alloy is refined along with prerefined bismuth-rich lead in an electrolytic lead refinery. The anode slimes,

which are rich in bismuth, are smelted directly to crude bismuth [17]. The flow sheet is shown in Figure 15.9. The intermediate products have the following compositions (%):

	Pb	Cu	Bi
Anodes	90–95 ^a	< 0.01	4–8
Cathodes	99.99	0.0003	0.001
Anode slimes	2–4	0.06	88–90

^aOr more.

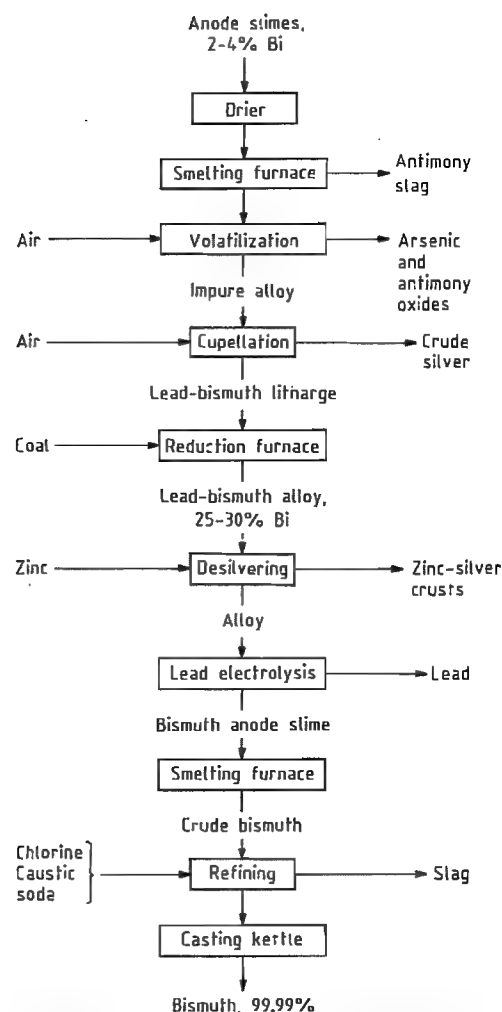


Figure 15.8: Bismuth recovery from lead anode slimes, Consolidated Mining and Smelting Co. of Canada [2].

15.5.3 Crude Bismuth from Copper and Tin Concentrates

Bismuth Separation from Copper Concentrates. Copper concentrates contain various amounts of bismuth. In g/t,

Gaspé, Québec	250
Skelleftea district, Sweden	700
Bathurst, New Brunswick [14]	200
Adrasman, Turkestan	several percent
La Oroya, Peru	400
Rokana, Sambia	200
Mufulira, Sambia	300

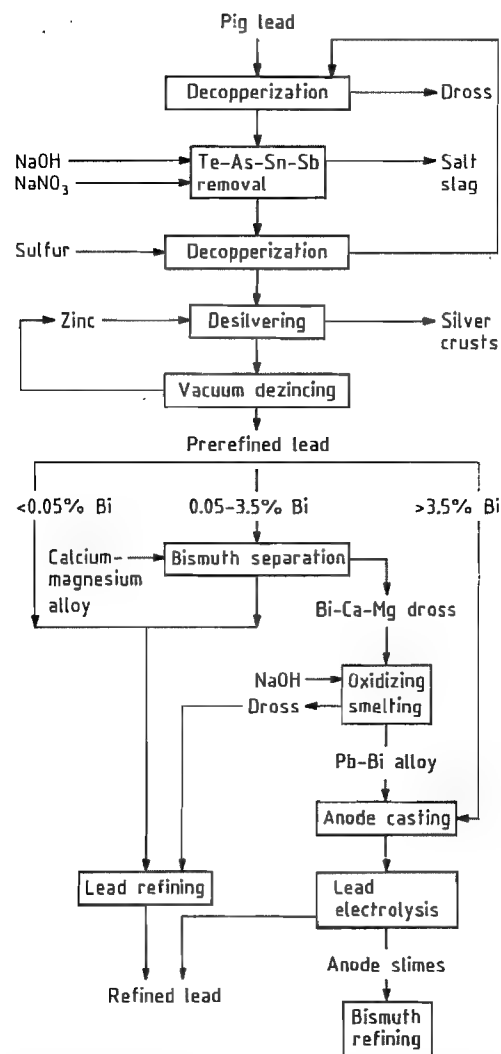


Figure 15.9: Simplified flow sheet of lead refining and bismuth separation at Norddeutsche Affinerie, Hamburg [17].

Åkulla and Kristineberg, Sweden 100-150
Rammelsberg, Harz 160

Most of the bismuth is volatilized during smelting of the concentrates, but the flue dusts are recycled to the smelting furnaces, at least in flash smelters, so that separation at this stage is not possible. In the following converter step the bismuth (more than 50%), along with Pb, Sb, and As, can be separated and enriched in the flue dust, which contains

several percent bismuth. After decopperization by leaching with sulfuric acid, these flue dusts are sent to lead smelters for further metal recovery. The bismuth distribution in various steps is shown in Table 15.6.

Separate treatment of the converter flue dusts is also possible. After decopperization, bismuth can be leached out selectively with H_2SO_4 -NaCl. It is precipitated as BiOCl [25].

The bismuth remaining in the blister copper is difficult to remove by distillation [26] or during copper electrolysis. The anode slimes contain considerable amounts of bismuth (Table 15.7), and treatment of these copper anode slimes enriches bismuth in the lead-bismuth litharge, which can be processed pyrometallurgically (Figures 15.7 and 15.8).

Table 15.6: Bismuth distribution (%) during copper smelting and converting.

	Sn	Pb	Bi	Ref.
Matte melting	matte	slag	flue dust	
	10	10	80	[24]
	35	15	50	[25]
Converting	blister copper	slag	flue dust	
	5	0	95-90-85	[24]
	10-15	0		[25]
Electrolysis	cathodes	anode slimes	electrolyte	
	≤ 5	30-60	65-35	[24]

Bismuth Separation from Tin Concentrates. Tin concentrates often contain bismuth. The bismuth can be leached with HCl and then precipitated as BiOCl , a process similar to the treatment of molybdenum concentrates [6].

In Vinto, Bolivia, the 0.5-5% bismuth is separated from the rich tin concentrates (55-63% Sn) by volatilization during a chloridiz-

ing roasting process in a multiple hearth furnace. Optimum volatilization occurs at 800-850 °C for an NaCl excess of only 25-50%. A retention time of ≈ 1 h leads to a volatilization exceeding 97%. The volatilized chlorides are absorbed in water and precipitated as BiOCl [27, 28].

If the bismuth is removed only partially or not at all from tin ores before reduction, it is reduced together with tin and can be separated with lead by vacuum distillation at ≈ 1150 °C and 10 Pa (0.1 mbar). The primary condensate is distilled again to give a secondary condensate. In this way the tin codistilled in the first distillation is recovered [29-32]. The rate-limiting step is evaporation at 1200 °C and diffusion at 1000 °C [29]. The extent of bismuth separation is shown in the following, all quantities in % [31, 32]:

	Sn	Pb	Bi
Crude tin	97	< 2	< 0.3
Primary condensate	50-60	10-40	3-30
Secondary condensate	2	80-90	< 20
Refined tin	> 99.97	< 0.02	< 0.01

15.6 Refining

Crude bismuth is always refined by pyrometallurgical methods, even though electrolytic refining is possible. The pyrometallurgical refining is almost identical with conventional lead refining consisting of the following steps:

- Decopperization by liquation and sulfuring
- Te, As, and Sb removal by addition of NaOH-NaNO₃, the Harris process

Table 15.7: Average content of copper anode slimes, % [19].

	Element							
	Se	Te	Ag	Cu	Pb	Sb	As	Bi
Rönnskär, Sweden	20	1	10	40	5	1	2	0.5
Rokana NCCM, Sambia	13	1	4.5	44	1	0.1	0.3	1.1
Kennecott Copper Corp., Garfield, UT	11-12	5	14	26	8.6	0.5	1.4	0.14
Mufulira RCM, Sambia	5	0.3	11-12	35-43	2-3	—	—	0.3
Port Kembla, New South Wales	3	2.5	6	18	10-25	8	7	0.4
Centromin, La Oroya, Peru	2.5	3	26	—	26	12	1.5	0.9
Anaconda Co., Great Falls, MT	1.5	6	28	14-20	4-5	2-4	4-5	0.2

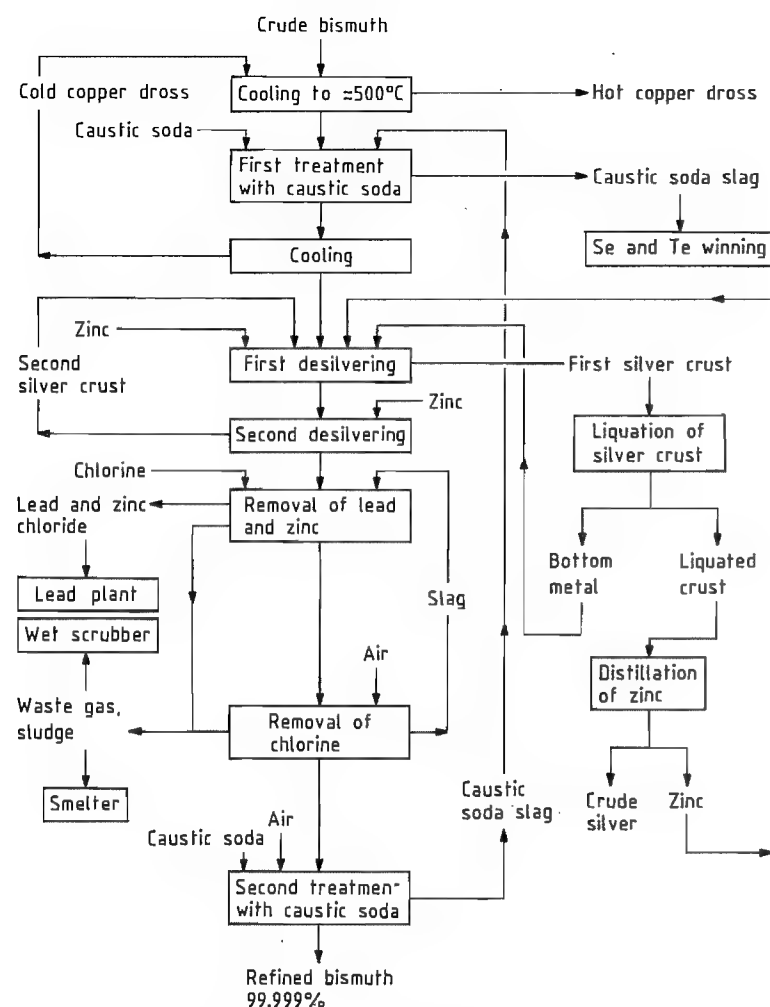


Figure 15.10: Refining of bismuth at Centromin, La Oroya, Peru [23].

- Removal of precious metals by Zn addition (Parkes process)
- Lead and zinc removal by chlorination
- Final oxidation with air in the presence of NaOH

With this procedure Norddeutsche Affinerie and Centromin produce 99.999% Bi. The residual impurities are 2 ppm Cu, 3 ppm Zn, and 2 ppm Fe. Figure 15.10 shows a typical flow sheet.

Liquation slightly above the melting point of bismuth removes copper and other impurities. Copper can be removed more effectively

if sulfur, soda, and charcoal are added. At 400–500 °C metal sulfides form, reducing the copper concentration to 10 ppm. The elements Se, Te, As, Sb, Sn, and Zn can be oxidized with NaNO_3 at 400 °C and dissolved in NaOH melt. Precious metals are removed by the addition of zinc, which forms an insoluble silver–zinc alloy. Just as in lead refining, removal takes place in two stages: liquation of rich and poor silver crusts. Approximately 12.5 kg Zn per tonne of Bi plus 2 kg Zn per kg of Ag are required, much greater amounts than in lead refining. The residual contents of Cu,

Ni, and Co are removed during desilvering, also by formation of insoluble alloys. After desilvering, bismuth contains more than 1% Zn and residual contents of lead, both of which can be reduced to a few ppm by chlorination at 400–500 °C. Excess chlorine can be blown out with air, or the bismuth can be washed with NaOH. Also copper, nickel, and cobalt can be removed from bismuth with chlorine [33]. The chlorination can be supported electrochemically: the bismuth melt, which is covered with a chloride melt, is the anode. Generally NaCl-CaCl_2 or KCl-ZnCl_2 melt is used. Lead and copper are converted into chlorides. Current densities can reach 0.4–0.8 A/cm^2 [34]. This multiple-step refining can be shortened considerably if the starting material is crust and dross from bismuth separation or anode slime from electrolytic lead refining. The quality of refinery bismuth is shown in Table 15.8.

Bismuth of *very high purity* is produced by vacuum distillation or zone melting. The starting material is always prerefined metal. Highest purities can be achieved by a combination of vacuum distillation and multiple zone melting. Vacuum evaporation at 800–850 °C and condensation at 650–750 °C refine bismuth almost completely. Al, Au, Ba, Be, Ca, Co, Cr, Fe, Ga, In, Ir, Li, Mo, Ni, Pd, Pt, Rh, Sn, Sr, Ti, and V stay in the residue. Cd, K, Na, Sc, and Zn evaporate but do not condense. Only a few elements cannot be removed: Ag, As, Mg, Pb, and Sb are insufficiently separated. Ce, Mn, and Tl follow the bismuth. At 800 °C the distillation rate is only 3.5 $\text{kgm}^{-2}\text{h}^{-1}$ and at 850 °C it is only 14 $\text{kgm}^{-2}\text{h}^{-1}$; 75–80% of the feed bismuth can be evaporated [35, 36].

Table 15.8: Composition of refinery bismuth [4].

	Bi, %	Contents, ppm				
		Cu	Ag	Zn	Pb	Fe
Centromin, La Oroya	99.999	2	—	3	—	2
Norddeutsche Affinerie, Hamburg	99.999	—	—	—	—	—
Cominco, Trail, Canada	99.999	—	—	—	—	—
Mitsui, Kamioka	99.99	6	9	—	10	—
San Gavino, Sardinia	99.99	10	15	—	10	—

Multiple zone melting of distilled bismuth produces very pure bismuth. Only 1 ppm of Ca, Pb, and Si and a total of 1.5 ppm of Al, Ca, Fe, and Mg are found.

Smelting bismuth with NaOH at 400 °C completely removes As, Sb, Sn, and Zn and almost completely slags Te and Pb. Careful chlorination before distillation and zone melting is recommended [37]. Treatment with chlorine removes Cu, Pb, Sn, and Zn completely. Zone melting then enriches Ag, Cu, Ni, Pb, Se, Sn, Tl, and Zn in the end piece of the rod.

15.7 Alloys

The binary systems of alkali metals or alkaline-earth metals with bismuth show intermetallic compounds with high melting points. In the system Bi–Li, for example, the compound Li_3Bi melts at 1145 °C. Some intermetallic compounds, especially those with K, Ca, and Mg, are or were used to separate bismuth from lead (see Section 15.5.2.1). The systems with Zn, Al, Ga, Co, or Si show limited solubility in the liquid phase. Bismuth and iron are insoluble in one another; therefore, iron equipment can be used for melting and refining the metal. The rare case of complete solubility in both the liquid phase and the solid phase appears in the system Bi–Sb. Some binary alloys, particularly those with Cd, In, Pb, Sn, and Tl, as well as some multicomponent alloys, form low-melting eutectics (Table 15.9). The most common ones, called fusible alloys, are offered under the trade names Asarco, Cerrolow, Cerrobend, Belmont, and Ostalloy.

Some multicomponent and some noneutectic compositions have both low melting points and the unusual characteristic of not contracting or even expanding on solidification. The alloy with 56% Bi, 20% Sn, and 24% Pb is said to have the largest volume expansion of any alloy [6]. Some alloys show effectively no volume change: 50% Bi–50% Pb and 70% Bi–30% Pb, for example.

Table 15.9: Fusible alloys [6, 38].

System	Eutectic composition, %	Eutectic temperature, °C
Cd-Bi	Cd 40, Bi 60	144
In-Bi	In 66.3, Bi 33.7	72
	In 33	109
	Bi 67	
Pb-Bi	Pb 43.5, Bi 56.5	125
Sn-Bi	Sn 43, Bi 57	139
Ti-Bi	Ti 23.5, Bi 76.5	198
	Ti 52.5, Bi 47.5	188
Pb-Cd-Bi	Pb 40, Cd 8, Bi 52	92
Sn-Cd-Bi	Sn 26, Cd 20, Bi 54	102
In-Sn-Bi	In 16, Sn 26, Bi 58	79
Ti-Pb-Bi	Ti 11.5, Pb 33.3, Bi 55.2	91
	Ti 48, Pb 9.8, Bi 42.2	186
Ti-Sn-Bi	Ti 14.3, Sn 35.7, Bi 50	124
	Ti 25, Sn 31, Bi 44	167
Pb-Sn-Cd-Bi	Pb 26.7, Sn 13.3, Cd 10, Bi 50	70
In-Cd-Pb-Sn-Bi	In 19.1, Cd 5.3, Pb 22.6, Sn 8.3, Bi 44.7	47
	In 4.0, Cd 9.6, Pb 25.6, Sn 12.8, Bi 48.0	64

Bismuth forms with alkali metals and alkaline-earth metals alloys that superconduct at low temperatures. Examples are LiBi, NaBi, CsBi₂, and BaBi₃. Their transition temperatures are 2.47 K, 2.22 K, 4.75 K, and 4.69 K, respectively.

Bismuth alloys are usually prepared by melting the components together, but prealloyed metals are used for the exact adjustment of the composition.

Bismuth is used as an alloy addition in steel and aluminum. The fabrication of low-carbon steel and stainless steel is improved by addition of 0.15% Bi and 2.2% Pb. To aluminum alloys 0.2–0.7% each of bismuth and lead are added [6].

Uses. The versatility of bismuth alloys results from their extremely low melting points and their volume changes on solidification combined with low viscosity and low surface tension. The composition can be chosen so that the alloy contracts, remains the same, or expands as a result of solidification. The last two cases, because they are unusual, are the most important.

The eutectic alloy Bi–Cd–In–Pb–Sn, melting at 47 °C, and some alloys melting higher

are used for the automatic release of fire alarm systems, automatic sprinkler systems, electric fuses, and safety plugs for storage tanks.

Thin-walled tubes and parts for the automobile and aviation industries are covered or filled up with bismuth alloy melting below 100 °C before bending or deforming to prevent collapse. After forming, the alloy can be melted out by dipping the part into boiling water. Especially suitable is the eutectic alloy Bi–Cd–Pb–Sn, which melts at 70 °C. It is very ductile and expands on solidification and during the first hour thereafter; therefore, it keeps the worked part under tension during bending or forming.

The noneutectic alloy with 48% Bi, 28.5% Pb, 9% Sb, and 14.5% Sn, which melts over the range 103–227 °C, expands greatly during the first hours after casting, reaching its final volume after ≈ 500 h. It can be used to grip tubes, tools, punches, and parts to be machined. Because it is diamagnetic, it is suited for embedding magnets in equipment or filling the space between magnets.

The noneutectic Bi–Sn alloy with 40% Bi and 60% Sn, which melts over the range 138–169 °C, contracts only 0.01% during solidification and aging. Such an alloy exactly reproduces the shape and dimensions of the casting mold. In sprayed parts it reproduces the base in every detail. This alloy is used for test casts, copies of irregular parts, molds for thermoplastic material in the rubber and plastic industry, and for meltable casting cores. The eutectic Bi–Sn alloy with 57% Bi, melting at 138 °C, expands 0.07% on solidification but contracts during the next 5 h. The final net expansion is only 0.02%. This alloy is used in dentistry for the production of models and molds [39].

Some bismuth alloys wet glass, mica, and enamelled ceramics. They are used to seal such substances to each other and to metals, as well as to produce high-vacuum seals for glass equipment. A so-called bismuth cement consists of 35% Bi, 37% Pb, and 25% Sn. Such alloys are used in holding devices for grinding and polishing glass and plastic lenses. Low-melting bismuth solders are used for the sol-

dering of temperature-sensitive electronic parts [40].

Cs–Bi alloys are used in photocathodes. The low conductivity of bismuth results in a good quantum yield. Bismuth tellurides and a bismuth–antimony alloy with 11% Sb are used in photoelectric infrared detectors. The compound Bi₂Te₃, especially its solid solutions with Bi₂Se₃ and Sb₂Te₃, is a useful thermoelectric material. The system AgSbTe₂–AgBiTe₂ also has interesting thermoelectric properties [41]. Mn–Bi alloys are permanent magnets [34].

In nuclear technology, bismuth and its alloys may be useful for cooling and as heat-exchange mediums because bismuth has an extremely low absorption cross section for thermal neutrons. However, nothing specific has been reported about use in modern reactors.

15.8 Compounds

In its inorganic compounds bismuth usually has 3+ or 5+ oxidation state. The 5+ oxidation state is a strong oxidation agent, e.g., NaBiO₆ or BiF₅. Bismuth has an oxidation state of 3– in a few intermetallic compounds, e.g., Li₃Bi and CaMg₂Bi₂. In gases, such as BiCl or BiO, in Bi(AlCl₄), and in alloy-like compounds, such as BiS or BiSe, bismuth can have 1+ or 2+ oxidation state, and 1+, 0, and 1– are present in polynuclear ionic species. However, the 1+ and 2+ states are rare, and compounds

with 4+ probably do exist also. On dissolution, bismuth compounds hydrolyze easily, yielding nearly insoluble basic salts of the type BiOX. In the presence of strong acids or in complexing agents, bismuth remains in solution. Table 15.10 shows some physical properties of the most important inorganic bismuth compounds.

Only a few inorganic bismuth compounds are produced commercially. Bismuth oxychloride is used in cosmetics. It is the basic ingredient of a pearly pigment found in eye shadow, hair sprays, powders, nail polishes, and other cosmetic products. Bismuth oxide can substitute for lead oxide in glass or porcelain.

Today the use of bismuth compounds in medicine is decreasing and the use of bismuth in pharmaceutical products is being viewed more and more as a questionable practice [42]. France, which in 1972 consumed more than 1000 t of bismuth, making it the largest bismuth consumer, has restricted the use of bismuth in pharmaceuticals, resulting in a sharp drop in bismuth consumption [43]. Bismuth compounds have been used because of their astringent, antiphlogistic, bacteriostatic, and disinfecting actions. In dermatology bismuth subgallate is still used in vulnerary salves and powders as well as in antimycotics. Medicines for depigmentation can no longer contain bismuth. Even bismuth subcarbonate, bismuth subnitrate, or the recently developed complex bismuth citrates ought not be used for the treatment of gastric disturbances.

Table 15.10: Physical properties of inorganic bismuth compounds.

Compound	Formula	Gibbs free energy of formation, kJ/mol	Density, g/cm ³	mp, °C	bp, °C
Bismuth tribromide	BiBr ₃	–263.8	5.72	219	461
Bismuthyl carbonate	(BiO) ₂ CO ₃	—	8.15	decomp.	—
Bismuth trichloride	BiCl ₃	–379.3	4.76	233.5	440.1
Bismuth chloride oxide	BiOCl	–374.3	7.72	232.5	447
Bismuth trifluoride	BiF ₃	–883.4	7.90	227	405
Bismuth pentafluoride	BiF ₅	—	5.40	151.4	230
Bismuth triiodide	BiI ₃	–333.5	5.80	408.5	542
Bismuth trinitrate pentahydrate	Bi(NO ₃) ₃ ·5H ₂ O	—	2.80	75	decomp.
Bismuth trioxide	Bi ₂ O ₃	–575.7	9.32	824	1890
Bismuth trisulfide	Bi ₂ S ₃	–176.7	6.81	747	—

Bismuth Tribromide, BiBr_3 . Golden-yellow crystals, cubic, hygroscopic. Prepared by reaction of the elements at 250 °C [44] or in methanol [45], by reaction of bismuth with molten iodine bromide and extraction with CCl_4 [46], or by dissolving Bi_2O_3 in concentrated hydrobromic acid, drying, and distillation in a stream of nitrogen. Bismuth tribromide is soluble in acetone, ether, acetic acetate, glacial acetic acid, and aqueous solutions of HCl , KCl , KBr , and KI . In water it hydrolyzes to BiOBr . It is insoluble in alcohol and carbon disulfide.

Bismuthyl Carbonate, $(\text{BiO})_2\text{CO}_3$. Naturally occurring as bismutite. White powder, sensitive to light, decomposition during heating. Preparation by precipitation with sodium or ammonium carbonate from nitrate solutions [47, 48].

Bismuth Trichloride, BiCl_3 . White powder, cubic, very hygroscopic. Prepared by chlorination of the molten metal [44] or by dissolution of the metal in aqua regia, boiling down, and distillation. *Bismuth chloride oxide*, bismuth oxychloride, BiOCl , is formed by heating BiCl_3 in air or by hydrolysis of BiCl_3 . The oxychloride is a white, lustrous, crystalline powder, ρ 7.72 g/cm³, that is practically insoluble in water, ethanol, acids, and bases. Hot concentrated alkali solutions convert it into the trioxide.

Bismuthine, BiH_3 . Bismuthine is a colorless gas unstable at room temperature. Prepared by treating Mg_3Bi_2 with dilute acids [49], decomposition of methylbismuthine or dimethylbismuthine [50], or reaction of bismuth halides with LiAlH_4 in a vacuum [3].

Bismuth Trifluoride, BiF_3 . White, fine powder, rhombic. Prepared by dissolving Bi_2O_3 in hydrofluoric acid [51] or by precipitation from an aqueous solution of bismuth trinitrate with aqueous KF or NaF [52]. Soluble only in acetone and liquid organic acids, insoluble in water. *Bismuth fluoride oxides*, $\text{BiO}_x\text{F}_{3-2x}$, form when BiF_3 is heated in air at 670–850 °C.

Bismuth Pentafluoride, BiF_5 . White needles, formed by fluorination of bismuth metal or

BiF_3 at 500 °C [53]; strong oxidant, violent reaction with water.

Bismuth Triiodide, BiI_3 . Greenish-black crystalline powder. Prepared by heating stoichiometric quantities of the elements in a sealed vessel at 150–180 °C [54] or by reaction of concentrated hydriodic acid with a solution of BiCl_3 in hydrochloric acid [55]. Insoluble in cold water. Boiling BiI_3 with water produces BiOI . Bismuth triiodide is soluble in alcohol, natural gasoline, xylene, and toluene. Red triammine complexes are formed in aqueous ammonia. The yellowish-orange Dragendorff reagent, KBiI_4 , for precipitating alkaloids, is formed by dissolving BiI_3 in potassium iodide solution.

Bismuth Trinitrate Pentahydrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Colorless, columnar crystals. Prepared by dissolving bismuth metal, Bi_2O_3 , or $(\text{BiO})_2\text{CO}_3$ in nitric acid [56]. Hydrolyzes in water to basic salts. The nitrate is soluble in strong inorganic acids, glacial acetic acid, and glycerol. It is the starting material for basic bismuth nitrates of composition $x\text{Bi}_2\text{O}_3 \cdot y\text{N}_2\text{O}_5 \cdot z\text{H}_2\text{O}$. Bismutum subnitricum, approximate composition $6\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, was commonly used for medical purposes.

Bismuth Oxides. Bismuth trioxide, Bi_2O_3 , is the only bismuth oxide which has been isolated in a pure state. There is also a Bi_2O_5 , but its characteristics are not yet well defined. Information about other oxides and related compounds is scarce.

Bismuth trioxide, Bi_2O_3 , is prepared by oxidation of bismuth metal at 750–800 °C, by thermal decomposition of carbonates, or by addition of alkali-metal hydroxides to a bismuth salt solution. In the last case hydrated bismuth trioxide precipitates. This gelatinous compound is usually represented by the formula $\text{Bi}(\text{OH})_3$; calcining it yields Bi_2O_3 .

Monoclinic $\alpha\text{-Bi}_2\text{O}_3$ converts in an endothermic transition at 710–740 °C to the high-temperature cubic modification $\delta\text{-Bi}_2\text{O}_3$, which is stable between 710 °C and the melting point. The transition is reversible, and $\delta\text{-}$

Bi_2O_3 is not stable at room temperature. Quenching thin layers of molten Bi_2O_3 forms metastable tetragonal $\beta\text{-Bi}_2\text{O}_3$, which converts back to $\alpha\text{-Bi}_2\text{O}_3$ when heated. This metastable $\beta\text{-Bi}_2\text{O}_3$ dissolves oxygen in its lattice without a structure change, the composition can range from $\text{BiO}_{1.50}$ to $\text{BiO}_{1.75}$. Heating $\beta\text{-BiO}_{1.50}$ to 750 °C and quenching at a moderate rate forms metastable cubic $\gamma\text{-Bi}_2\text{O}_3$, which contains more oxygen than the stoichiometric formula Bi_2O_3 expresses. The preparation of all these modifications is described in detail in [3]. Quenching molten mixtures of Bi_2O_3 and other metal oxides from 800–1000 °C to 0 °C produces stabilized $\delta\text{-}$ and $\beta\text{-}$ modifications; tempering for 24 h at 600 °C yields a $\gamma\text{-}$ modification contaminated with other oxides.

Bismuth trioxide is soluble in strong inorganic acids and concentrated alkaline solutions containing glycerol. Above 710 °C it attacks metal oxides; in fact, molten bismuth trioxide dissolves every metal oxide and even corrodes platinum.

Bismuth trioxide monohydrate, $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$, is a white powder. Its composition and constitution are not completely elucidated. $\text{Bi}(\text{OH})_3$ and BiOOH probably do exist. A hydrated oxide precipitate is formed by reaction of an acidic bismuth nitrate solution with ammonia or caustic soda solution [57].

Bismuth pentoxide, Bi_2O_5 , is prepared by oxidizing suspended Bi_2O_3 with Cl_2 , Br_2 , or H_2O_2 in an aqueous alkaline solution. Each of these reactions goes almost to completion. Molten mixtures of Bi_2O_3 and alkali-metal oxides can be oxidized by air or oxygen. The reaction is favored by excess alkali. The excess alkali can be stripped with methanol at 0 °C to form yellowish-orange sodium metabismuthate, NaBiO_3 . Addition of nitric or perchloric acid leads to a compound whose composition varies from $\text{Bi}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ to $\text{Bi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. Both compounds are strong oxidants.

Bismuth Trisulfide, Bi_2S_3 . Naturally occurring as bismuth glance. Dark brown to grayish black, metallic luster, rhombic. Prepared by heating bismuth with sulfur or bismuth trioxide with sulfur compounds or by precipitation

from aqueous bismuth(III) solutions with H_2S . It is insoluble in water and alkaline solutions but soluble in hot aqueous salt solution or concentrated nitric acid. Concentrated alkaline metal sulfide solutions or melts dissolve Bi_2S_3 to form compounds of the type KBiS_2 . Similar compounds naturally occur with copper, silver, and lead.

15.9 Chemical Analysis

For qualitative determination bismuth [58] is precipitated as Bi_2S_3 from slightly acidic solution with H_2S . The precipitate is brown black and soluble in strong acids and hot dilute nitric acid. Yellow-green Bi_2S_3 precipitates from alkaline solution on addition of Na_2S . Bismuth can be precipitated by hydrolysis from hot dilute hydrochloric acid as bismuth oxychloride, provided excess chloride ions are absent. Aqueous ammonia precipitates bismuth as white bismuth oxide hydrate, which can be reduced to bismuth metal with alkaline stannate(II) solution.

Bismuth phosphate, BiPO_4 , can be precipitated quantitatively from very dilute nitric acid solution. Bismuth in medicinal preparations is determined by precipitation as basic bismuth carbonate. Calcining at 550 °C yields Bi_2O_3 . A thiourea–bismuth mixture is of yellow color in nitric acid solution, and this is the basis for a photometric method. If ions such as Fe , Hg , Zr , etc., are absent, titration with EDTA is a selective, quantitative, and fast method of bismuth analysis. This method has become very popular [59]. Emission, mass, of atomic absorption spectrometry allow detection of less than 1 ppm Bi .

15.10 Economic Aspects

Bismuth concentrates are a by-product of nonferrous metal ore dressing. The metal available from concentrates has remained nearly the same, between 3600 and 4600 t/a since the 1960s. The world's one and only bismuth mine, Telamayu in Bolivia, which had produced about 15% of the worldwide supply,

stopped production in 1980 because of either declining demand or perhaps total exhaustion of the site. Also Australia and Peru are reducing their production. Only a part of bismuth refining is carried out in the mining countries. Table 15.11 shows the metal content of bismuth ores and concentrates, corresponding closely to the world production of 3795 t in 1980. The main producer of bismuth metal is the United States, producing ≈ 950 t/a [61]. Bismuth suppliers are listed in [63].

Bismuth (99.99%) is quoted in London and New York in \$/lb (1 lb = 0.454 kg). After rising to \$9/lb in 1974 the price of bismuth fell steadily for years. The price was \$1.67 per pound in December, 1983. However, since then the price has increased, to \$6.60 in February, 1985. The prices are much higher for high-purity bismuth (99.999%). Table 15.12 shows actual U.S. bismuth consumption. No consumption data for the European market have been published for several years. Because of substitution and regulatory restrictions bismuth consumption has decreased more in Europe than in the United States.

Table 15.11: Bismuth in ores and concentrates, t [60–62].

	1970	1973	1977	1980
Australia	363	500	912	907
Bolivia	567	690	680	11
Canada	272	300	165	171
China	200*	250	249	259
France	59	65	66	59
Germany	18	20	10	9
Italy	23	25	15	10*
Japan	68	75	80*	80*
Mexico	453	600	729	748
Peru	816	690	590	522
Romania	9	10	80	80*
South Korea	136	150	134	90*
Sweden	32	35	15	15*
Former USSR	50*	50	66	73
United States	363	400	400	400*
Former Yugoslavia	108	120	74	73
Others	204	320	399 ^b	215 ^b
Total	3741	4300	4664	3722

* Estimated.

^b Calculated.

Table 15.12: Bismuth consumption in the United States, t [61].

	1970	1973	1978	1980
Chemical industry*	567	543	521	556
Fusible alloys	292	423	379	291
Metallurgical additions	236	376	210	211
Other alloys	6	7	10	11
Others	5	5	8	7
Total	1106	1354	1128	1076

* Including pharmaceutical products and cosmetics.

15.11 Toxicology of Bismuth and Bismuth Compounds

Poisoning by bismuth and bismuth compounds has occurred more frequently during medical therapy than by exposure at the workplace [64]. It resembles poisoning caused by lead and mercury and their compounds. After oral administration, water-insoluble bismuth compounds, such as bismuth nitrate oxide, $\text{BiO}(\text{NO}_3)$, are hardly absorbed, and acute poisoning is seldom. Increased absorption was observed, however, when large quantities of such compounds were applied to skin lesions, resulting in serious poisoning, sometimes fatal. Water-soluble bismuth compounds are absorbed quickly, and acute poisoning is likely to occur. However, the relatively high toxicity of bismuth nitrate oxide, which was observed especially in children, is most likely not caused by bismuth but by reduction of nitrate to nitrite and subsequent methemoglobin formation by intestinal bacteria.

The main hazard of bismuth is the chronic exposure that took place during long-term therapy (up to 30 years in some cases) practiced earlier. Such exposure can have serious consequences for humans and animals. First symptoms of chronic intoxication by bismuth are hypersalivation, stomatitis, and a grayish black seam surrounding the gums (symptoms similar to those caused by lead).

According to many investigations, e.g., [65] and [66], long-term oral administration caused encephalopathies accompanied by distractions, ataxia, myoclonic spasms, insomnia, and headache in many cases and less frequently epileptic attacks. Some cases ended in

death, the brains of the deceased containing large quantities of lipid-soluble bismuth compounds [67]. This crossing of the blood-brain barrier by bismuth compounds was demonstrated in other experiments, e.g., for trivinylbismuth in pigs [68]. In another epidemiological study, a group of patients with manifest bismuth poisoning was compared to a control group that had been exposed to the same amount of bismuth but that did not show any symptoms of poisoning [69]. The investigators concluded that bismuth poisoning is caused by the transformation of bismuth compounds of low toxicity into those of high toxicity by intestinal bacteria.

The occurrence of osteolytic and osteonecrotic arthropathies of the shoulder was pointed out in [70]. In over 59 cases of bismuth poisoning, bone lesions accompanied by encephalopathies were described [71]. Caused by the elimination of bismuth compounds in the urine, albuminuria and nephritis were observed also [64]. Bismuth also causes eye defects [72], which was confirmed by experiments with mice [73]. Inhalation of trimethylbismuth, $\text{Bi}(\text{CH}_3)_3$, by humans causes irritations of the respiratory tract and conjunctivas. Cats and dogs that inhaled trimethylbismuth for 10–20 min showed ataxia, restlessness, and convulsions; after 24 h severe encephalitis was observed [74].

In a long-term carcinogenicity test bismuth chloride oxide, BiOCl , was fed to rats over a period of two years (1, 2, and 5% in the feed) [75]: neither carcinogenic nor other toxic effects that were caused by bismuth chloride oxide could be found. So far there is no evidence for carcinogenicity, mutagenicity, and teratogenicity of bismuth compounds [76].

The following toxicological data are available for bismuth and bismuth compounds: lowest published lethal dose for bismuth, 221 mg/kg (humans, presumably oral) [77]; bismuth chloride oxide, BiOCl , LD_{50} 22 g/kg (rat, oral); trimethylbismuth, $\text{Bi}(\text{CH}_3)_3$, LD_{50} 484 mg/kg (rabbit, oral), LD_{50} 182 mg/kg (rabbit, subcutaneous), LDLo 11 mg/kg (rabbit, intravenous) [74]. In the Swiss list of toxic substances bismuth nitrate oxide, BiONO_3 ,

and triphenyl bismuth, $\text{Bi}(\text{C}_6\text{H}_5)_3$, are in class 3; bismuth titanate, $\text{Bi}_2(\text{TiO}_4)_3$, is in class 5.

15.12 Pigments

Bismuth-containing special effect pigments based on platelet-shaped crystals of bismuth oxide chloride (bismuth oxychloride, BiOCl) have been known for a long time (see Section 15.12.5). More recently, greenish yellow pigments based on bismuth orthovanadate, BiVO_4 , have attracted increasing interest. They represent a new class of pigments with interesting coloristic properties, extending the familiar range of yellow inorganic pigments (iron yellow, chrome yellow, cadmium yellow, nickel titanium yellow, and chromium titan yellow). In particular they are able to substitute the greenish yellow shades of the lead chromate and cadmium sulfide pigments.

Historical Aspects. Bismuth vanadate occurs naturally as the brown mineral pucherite (orthorhombic), as Clinobisvanite (monoclinic) and as Deyerite (tetragonal). Its synthesis was first reported in 1924 in a patent for pharmaceutical uses [78]. The development of pigments based on BiVO_4 began in the mid 1970s. In 1976, Du Pont described the preparation and properties of “brilliant primrose yellow” monoclinic bismuth vanadate [79]. Montedison developed numerous pigment combinations based on BiVO_4 [80]. Pigments containing other phases besides BiVO_4 , e.g., Bi_2XO_6 ($\text{X} = \text{Mo}$ or W), have been reported by BASF [81] and became the first commercial product (trade name Sicopal® Yellow L1110). Since then Bayer [82], Ciba-Geigy [83], BASF [84], and others have published further methods for the manufacture of pigments based on BiVO_4 . On the market are now pigments for the use in paints and plastics of the following suppliers: BASF, Ciba-Geigy, Bayer, Capelle, Bruchsaler Farbenfabrik, and Heubach.

Recently, BASF placed a new reddish yellow bismuth vanadate pigment on the market (trade name Sicopal® Yellow L 1600).

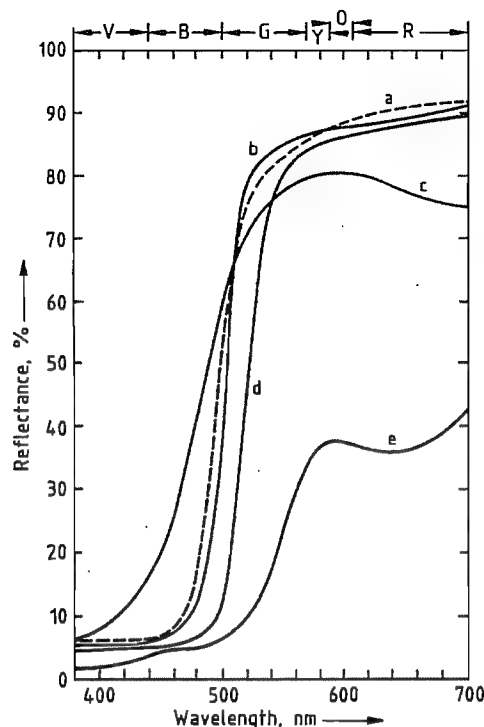


Figure 15.11: Reflectance curves of yellow pigments: a) BiVO_4 ; b) CdS ; c) $(\text{Ti, Ni, Sb})\text{O}_2$; d) $\text{PbCrO}_4\text{-PbSO}_4$; e) FeOOH .

15.12.1 Properties

Most of the commercial bismuth vanadate pigments are now based on pure bismuth vanadate with monoclinic structure, though there are still pigments based on the two-phase system bismuth vanadate molybdate, $4\text{BiVO}_4 \cdot 3\text{Bi}_2\text{MoO}_6$. The pure bismuth vanadate pigments show a higher chroma than the two phase systems. In the following the physical and coloristic properties of a pure bismuth vanadate pigment are given (Sicopal® Yellow L 1100, BASF):

Density	6.1 g/cm ³
Refractive index n	2.45
Specific surface area (BET)	13 m ² /g
Oil absorption	33 g/100 g of pigment
Composition: Bi	64.51%
V	15.73%
O	19.76%

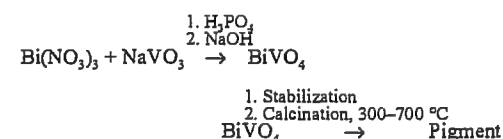
Bismuth vanadate, C. I. Pigment Yellow 184, is a pigment with a greenish yellow co-

lour, having high tinting strength, high chroma, and very good hiding power. When compared with other yellow inorganic pigments, it most closely resembles cadmium yellow and chrome yellow in its colouristic properties (Figure 15.11). Bismuth vanadate shows a sharp increase in reflection at 450 nm and considerably higher chroma than iron yellow or nickel titanium yellow. It has very good weather resistance both in full shade and in combination with TiO_2 . Pigment properties follow:

Hue angle H° (HGD, hue grade; CIELAB)	93.7
Chroma C^*ab (CIELAB)	95.5
Hiding power	at 42.5% by weight in dry film about 70 μm over black/white
Weather resistance (DIN 54002)	alkyd/melamine
Full shade	4-5
Mixed with TiO_2 , 1:10	4-5
Chemical resistance in crosslinked paint films	
acid	5 (2% HCl)
alkali	5 (2% NaOH)
Heat stability	> 200 °C

15.12.2 Production

The production process for bismuth vanadate pigments consists usually of a precipitation reaction followed by a calcination step. The calcination step is different from producer to producer and can be completely absent depending on the precipitation process and the desired product properties.



In this process first, a fine precipitate is formed by adding an alkaline solution of sodium or ammonium vanadate to an acidic bismuth nitrate solution in presence of a considerable amount of phosphate or, in the inverse process, by adding the bismuth nitrate solution to a sodium or ammonium vanadate solution. Thereafter, the pH is set between 5 and 8 with sodium hydroxide and the precipitate crystallizes to monoclinic bismuth orthovanadate usually by heating to reflux. After

this crystallization, the pigment is often coated with calcium or zinc phosphate or aluminum oxide to improve the lightfastness and weather-resistance. The final process is usually the calcination followed by wet milling and spray drying. The spray drying process produces a fine granulated dust-free pigment.

For the use in plastics, the pigment is additionally coated with silica and other components to increase the heat stability in certain polymers, like polyamide, up to 320 °C.

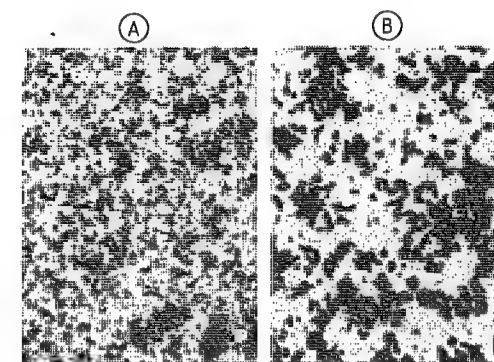


Figure 15.12: Particle size after precipitation (A) and subsequent heating (B) (magnification $\times 6000$).

15.12.3 Uses

Bismuth vanadate pigments are used in the manufacture of lead-free, weather-resistant, brilliant yellow colors for automobile finishes and industrial paints. They are suitable for the pigmentation of solvent-containing paints, water-based paints, powder coatings, and coil-coating systems. It can be mixed with other pigments especially to produce brilliant colours in the orange, red, and green regions like the german standard colors RAL 1021, 1028, 2004, 3020, 6018, and 6029.

Recently, different producers have developed bismuth vanadate pigments for the use in plastics. These pigments are used in every type of polymer, especially in polyethylene and technical plastics.

The annual production of bismuth vanadate pigments is now about 500 t. In the near future an increasing market of 1000 to 2000 t/a is expected.

15.12.4 Toxicology

Bismuth vanadate pigments are acute toxic neither on inhalative nor oral incorporation. They show chronic toxicity on inhalation due to the vanadium content. The "no-effect level" for rats is 0.1 mg/m³ (exposure: 3 months, 6 hours/day, 5 days/week). The critical factor for the inhalation toxicity is the real amount of pigment in the lungs, and not just the concentration in air. Because of the high density of the pigment and because the supply form is a fine granulate the risk of inhalation is very low. Therefore the dust-free pigments can be handled under usual hygienic working conditions [85].

15.12.5 Bismuth Oxychloride

[86-96]

Bismuth oxychloride, BiOCl , is, besides natural pearl essence and basic lead carbonate, one of the classic pearlescent pigments.

Powders containing bismuth compounds have long been used for decorative purposes to generate a shiny luster or lustrous colors (e.g., facial cosmetic powders in ancient Egypt, imitation pearls made by coating glass and ceramic beads). Bismuth oxychloride was the first synthetic nontoxic nacreous pigment. It is produced by hydrolysis of acidic bismuth solutions in the presence of chloride ions. Precipitation conditions may be varied (concentration, temperature, pH, pressure) or surfactants added to obtain the desired crystal quality. The virtually tetragonal bipyramidal structure is thereby "squashed" into a flat platelet.

Pure BiOCl is available in three grades with different nacreous effects that depend on the aspect ratios and crystal size:

- Low- or medium-luster powder (aspect ratio 1:10 to 1:15), mainly used as a highly compressible, white, lustrous filler with excellent skin feel
- Dispersion of high luster quality (aspect ratio 1:20 to 1:40) consisting of square or octagonal platelets in nitrocellulose lacquers (nail polish) or castor oil (lipsticks)

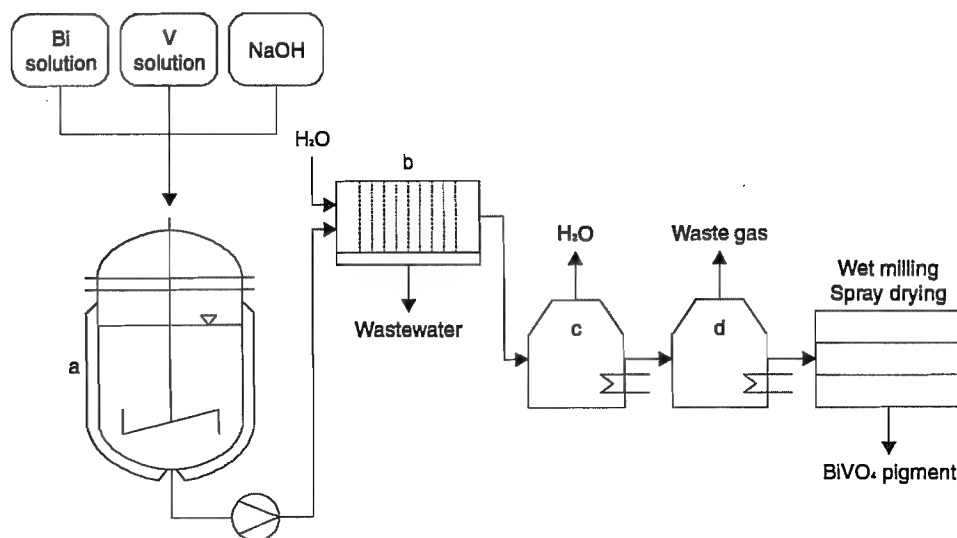


Figure 15.13: Flow diagram for the production of bismuth vanadate pigment: a) Reaction vessel; b) Filter; c) Dryer; d) Furnace treatment.

- Dispersion of very high luster quality (aspect ratio > 1:50) consisting of lens-shaped platelets in nitrocellulose lacquer, castor oil, or butyl acetate

Pigments consisting of BiOCl-coated mica or talc and blends of BiOCl with other organic or inorganic colorants are also available.

The dominant market for BiOCl is still the cosmetic industry. Its low light stability (it turns from silver white to metallic grey in sunlight), relatively high price, fast settling (high density, 7.73 g/cm³), and mechanical sensitivity limit its use in technical applications. Although the darkening reaction is not yet understood, low-luster grades with improved light stability are available. Some manufacturers promote the combination with UV stabilizers for technical purposes. Uses are in the button industry, bijouterie, printing, and for X-ray contrast in catheters. The current world market is ca. 500 t/a.

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16 Cadmium

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16.1 Introduction

Cadmium, atomic number 48, belongs to the zinc subgroup of the periodic table along with mercury. In its compounds it has an oxidation state of 2+. There are eight natural isotopes, with mass numbers ranging from 106–116. The most abundant are ^{114}Cd (29%) and ^{112}Cd (24%). There are also a number of metastable isotopes.

STROHMEYER discovered cadmium in 1817 in the course of investigating zinc carbonate. He recognized that the yellow color of a sample of zinc oxide produced by roasting was due to the presence of an unknown metal oxide. Because this new element also occurred in the zinc ore calamine, a name derived from the Latin word "cadmia", he named the new element cadmium.

Unlike some other heavy metals, such as lead or mercury, which have been used since ancient times, cadmium has been refined and utilized only relatively recently. After its discovery more than a century elapsed before the

metal or its compounds were employed to any significant extent. Only in the last 40–50 years have production and consumption risen distinctly. The primary uses today are electroplated cadmium coatings, nickel-cadmium storage batteries, pigments, and stabilizers for plastics. Publicity about the toxicity of cadmium has affected the consumption.

16.2 Properties

Cadmium is a soft, ductile, silver-white metal. Like tin, it makes a grating sound when bent. The most important physical properties are given below.

<i>mp</i>	320.9 °C
<i>bp</i>	767 ± 2 °C
Vapor pressure at	
218 °C	0.133 Pa
302 °C	6.666 Pa
392 °C	133.32 Pa
485 °C	1333.2 Pa
611 °C	13.332 kPa
727 °C	66.660 kPa
765 °C	101.33 kPa
Density	8.64 g/cm ³
Specific heat at 20 °C	0.230 Jg ⁻¹ K ⁻¹

Heat of fusion	55 J/g
Heat of vaporization at 767 °C	890 J/g
Thermal conductivity at 18 °C	$92 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$
Electrical resistivity at 18 °C	$7.5 \times 10^{-6} \Omega \text{ cm}$
Brinell hardness	22–24
Coefficient of linear expansion at 20 °C	$31 \times 10^{-6} \text{ K}^{-1}$
Ionization potential	8.96 V
Electrochemical potential	–0.40 V
Cross section for thermal neutrons	$2450 \times 10^{-28} \text{ m}^2$

The crystal structure is distorted closest packed hexagonal.

Cadmium is stable in air; only a slight loss in luster occurs after an extended period of time in air. When it is heated, initially yellow to brown colors develop as a thin oxide layer forms. If the metal is heated to volatilization, it burns with a red-yellow flame to form brown cadmium oxide, which is poisonous. Cadmium dissolves readily in nitric acid but only slowly in hydrochloric or sulfuric acid and not at all in bases. Zinc displaces it from solution.

16.3 Occurrence, Raw Materials

Cadmium is widely distributed. It occurs in the earth's crust with a content estimated to be between 0.08 and 0.5 ppm. In top soil cadmium content usually lies between 0.1 and 1 ppm.

The best known cadmium mineral is greenockite, cadmium sulfide (77.6% Cd). One mineral form of cadmium carbonate (61.5% Cd) was named otavite after its discovery site, the Tsumeb Mine, in the Otavi deposit of South-West Africa. In Sardinia, pure cadmium oxide (87.5% Cd) was found in a zinc deposit. However, none of these cadmium minerals is of industrial importance because the deposits are too small.

Only zinc minerals in which cadmium is found as an isomorphic component, with concentrations ranging from 0.05 to 0.8%, averaging about 0.2%, have economic significance for cadmium recovery [2]. In addition, lead and copper ores contain small amounts of cadmium, which can be separated during the roasting and smelting processes.

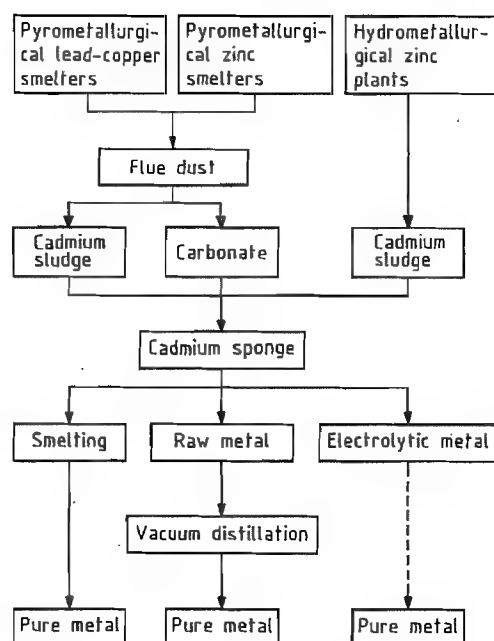


Figure 16.1: Processes for the production of cadmium metal.

16.4 Refining

Figure 16.1 summarizes the individual process steps and their combination. Detailed description, with emphasis on the distillation process, can be found in [3].

16.4.1 The Starting Materials

The flue dust on which the volatile cadmium collects when zinc, copper, and lead ores are heated in air are the primary starting material for cadmium recovery and refining. In many cases it is necessary to recirculate this dust to obtain higher cadmium concentrations [4].

In the Outokumpu Zinc Works in Finland, roasting material contains 0.19–0.24% Cd. The cadmium content is extracted in the third step of the zinc process and results in a cake consisting of 90% cadmium and 10% zinc. This is the starting material for further processing [5].

If the primary flue dust is reduced in a rotary oven, lead and zinc remain in the oven, while the cadmium is volatilized and enriched in the secondary flue dust.

In the Berzelius Metal Works, Duisburg, Germany, complex lead–zinc ores are refined by the Imperial smelting process. When the concentrate is roasted in the sintering furnaces, cadmium-containing flue dust is produced. This is leached in an acid solution, and the cadmium is subsequently precipitated as cadmium carbonate. The cadmium in secondary raw materials, such as steel mill dust, leaching sediments, and sludge from water treatment, can be processed at the same time. However, before they are mixed with the concentrates they are enriched in a rotating tube furnace (Waelz process).

In hydrometallurgical zinc refining, the cadmium-containing zinc concentrate is leached with sulfuric acid. The cadmium is removed from the solution together with copper by reduction with zinc dust to give a metallic sludge. Similar cadmium sludges form in the purification of zinc solutions used in the production of zinc sulfide pigments or zinc carbonate. These cadmium sludges are the most important starting materials for cadmium refining today. The secondary starting materials mentioned above can be added to the primary raw materials without causing large alterations in the refining process.

Also of economic significance is the recycling of used nickel–cadmium storage batteries; cadmium-containing alloys, such as Sn–Cd metallizing alloys from the manufacture of rectifiers; defective industrial batches; residues from the production of cadmium pigments; and cadmium-containing fluorescent materials. Special processes are usually necessary to convert the cadmium content into a form that can be processed normally. The most important processes of this type are discussed in Section 16.4.6.

16.4.2 Leaching of the Starting Materials and Cementation

Cadmium is extracted from the enriched starting materials by oxidizing solutions. The extraction must be carried out in such a way that all the cadmium as well as the zinc dissolves. The procedure of Ruhr Zinc, Datteln, Germany, is described here as an example. The liquid from electrolytic baths, which has a sulfuric acid concentration of 25–30 g/L, is conveyed into 50-m³ tanks. In order to oxidize the cadmium, either air is blown in or manganese dioxide is added. Fresh cadmium sludge or cadmium carbonate is added to decrease the acidity of the solution, and a copper-containing precipitate is removed with a filter press. Zinc, cadmium, and thallium are almost completely dissolved in the solution along with almost no copper, cobalt, nickel, and arsenic [6].

Copper chloride mixed with other metal chlorides or iron(III) chloride can be used as an oxidant instead of air [7, 8]. Dust from the sintering process can also be roasted to give sulfates and then be extracted in a similar fashion with water [9].

Independent of the further processing of the cadmium, it is precipitated from the solution as a metal sponge by reduction with zinc. It is necessary the solution is purified first.

The cadmium raw solution resulting from the leaching step at Ruhr Zinc contains about 30 g/L of zinc and small amounts of cobalt, nickel, thallium, and copper in addition to the 30–40 g/L of cadmium. The cadmium is precipitated in a 50-m³ tank at a temperature of 60 ° in order to avoid excess zinc in the cadmium sponge, only 80% of the stoichiometric amount of the zinc is added initially. The remaining zinc dust is added in small portions until the cadmium concentration of the solution is below 0.1 g/L. After decanting, the cadmium sponge is left in the reaction container. The precipitation is carried out three times, principally to reduce the amount of zinc. After the final precipitation, the sponge is washed, and the wash water is recycled to the zinc plant. The precipitated sponge contains 90% cadmium and only 2–5% zinc [6].

The procedure of the Outokumpu Zinc Works starts with a purified cadmium solution because of the nature of the succeeding metal recovery (see Section 16.4.5). Copper is removed with zinc powder, and lead is removed with barium carbonate. The separation of the cadmium sponge from the solution, however, scarcely deviates from the Ruhr Zinc processes. The greatest difference is that the cementation is interrupted at cadmium concentrations of 3–5 g/L, and the solution recirculated. Together with a very careful wash, this reduces the residual content of zinc in the compacted cadmium-sponge briquettes to 0.5–2.0% [5].

16.4.3 Electrolytic Recovery

Today, the largest amounts of cadmium are recovered electrolytically. It is customary to extract the cadmium sponge in the same tank with the cadmium-containing electrolytic acid. Air is supplied at a temperature of 80 °C for 6–10 h. Concentrated sulfuric acid is added to keep the concentration of free sulfuric acid at 100 g/L. Manganese dioxide can also be used as oxidant [6].

The time required to dissolve the cadmium sponge at room temperature can be reduced by blowing air through special reactors. The relationship between solid and liquid, the amount of air, and the pH are carefully controlled to reduce the time and temperature required for the dissolution [10].

The electrolytic deposition of cadmium requires that the impurities that cause problems during the electrolysis or that are deposited as impurity with cadmium be removed prior to electrolysis. Traces of copper can be removed by addition of small quantities of sodium sulfide in the form of copper sulfide or by cementation with zinc dust. Thallium is removed as thallium dichromate by addition of potassium dichromate. Thallium can also be removed as thallium(III) hydroxide by addition of potassium permanganate. Any arsenic is eliminated as iron arsenate by oxidation with the potassium permanganate. The lead remaining

in solution is removed by adding strontium carbonate to occlude lead carbonate [6].

The anode consists of lead, which does not dissolve, and the cathode is sheet aluminum. Today rotating cathodes, which allowed high current density, have disappeared because current densities of 100 A/m², permitting economic electrolysis, can also be attained with fixed cathodes. However, the cathode deposit must be stripped after 12-h intervals to avoid low yields caused by short circuits between cathode and anode. The current yield is ≈ 93%; the energy consumption is 1250 kWh per tonne of cadmium cathode sheet deposited. Careful operation and the use of hide glue and sodium silicate allow cadmium of high purity to be produced. Typical impurity levels in electrolytic cadmium sheet are 5–10 ppm Cu, 15–20 ppm Pb, 5–10 ppm Tl, and 5 ppm Zn.

Some sheet is used as is. Otherwise, it is melted under a cover of sodium hydroxide to prevent oxidation and to reduce the amount of zinc. The molten metal is poured into molds to produce marketable shapes.

16.4.4 Distillation

After mixing with a reducing agent such as pulverized coke, the cadmium sponge can be briquetted. The briquettes can be distilled under atmospheric pressure to a raw metal still containing thallium and zinc. These impurities can be separated from the fused metal by addition of ammonium chloride and caustic soda. Distillation under reduced pressure avoids a number of disadvantages of distillation at atmospheric pressure. The differences between the vapor pressure of cadmium and those of the most important accompanying elements allows Preussag (Germany) to produce a 99.99% pure metal in a single step. The raw cadmium can contain up to 3% lead and thallium as well as 1% copper [11]. Every hour, 100 kg of pure cadmium is produced at a distillation pressure of 0.7–2.7 kPa and a temperature of 420–485 °C. The presence of thallium, the most volatile impurity, at a concentration exceeding 10 ppm in the distillate

indicates that the distillation is not functioning properly.

The cadmium distillation process of Hoboken Overpelt, Belgium, allows the processing of cadmium–zinc alloys containing 15–20% Zn. In a two-step distillation procedure, both zinc and cadmium are obtained highly pure (99.995%) [12].

16.4.5 Other Processes

The cadmium sponge of the Outokumpu Zinc Works contains 0.5–2% zinc, 13 ppm lead, and 15 ppm copper. The briquettes pressed out of this material are smelted with sodium hydroxide. In seven hours 2.2 t of cadmium is obtained using a 110-kW furnace. The refined metal is drawn in a continual casting machine to a cadmium wire, which is then cut to rod. These cadmium rods have a purity of at least 99.95%; the impurities (max.) consisting of 20 ppm Cu, 10 ppm Zn, 5 ppm Tl, 5 ppm Fe, and 15 ppm Pb [5].

The removal of cadmium from solution by ion exchange has been described [13]. After stripping, the cadmium is processed further by cementation and smelting. Complexation of the cations to give anionic cadmium species allows selective separation of the cadmium even from copper and iron [14]. Aliphatic carboxylic acids [15] and *o*-aminomethylphenols [16] selectively extract cadmium from aqueous solution.

16.4.6 Recycling

The purpose of the recycling procedures described here is the production of intermediate products by special procedures that can then be fed into the normal cadmium production processes.

The recovery of *cadmium–tin alloys*, about 65% Sn and 35% Cd, usually begins by dissolving the scrap in nitric acid. The tin stays in the residue as stannic acid. An impure carbonate is precipitated from the cadmium nitrate solution with soda.

The residue and the rejected batches from the production of *cadmium pigments* contain-

ing cadmium sulfide and selenide are dissolved in strongly oxidizing acid. The cadmium is recovered by cementation or as the carbonate. A variation of this process is described in [17].

In order to recycle the cadmium from *nickel–cadmium batteries* and similar production scrap, the parts are dissolved in agitated 2% sulfuric acid. A reasonably good separation from the dissolved nickel can be attained by taking advantage of the lower stability of the ammine complexes of cadmium: cadmium can be precipitated from ammonium hydroxide solution as carbonate, whereas nickel remains in solution [18]. Alternatively, nickel can be extracted from the ammonia solution with chelating reagents before cadmium carbonate is precipitated [19].

Sludge from the treatment of cadmium-containing waste water can often be injected directly into the refinery process (Section 16.4.1). Preliminary, conventional wet chemical enrichment is possible but is usually omitted for economic reasons [20]. Several methods for conversion of electroplating waste water to sludge not requiring special handling can be found in [21].

A plant was constructed by Sab-Nife in Sweden for recycling used batteries and scrap at the same location where nickel–cadmium batteries are produced. Cadmium-containing waste and filter dust are leached with acid, and the cadmium is deposited by electrolysis. Used batteries are dismantled in a semiautomatic process. From the iron- and cadmium-containing plates, the cadmium is distilled under a reducing atmosphere at 850 °C and returned to the production department. Even sealed cells can be processed by distillation after the plastic is destroyed by pyrolytic pretreatment in a slightly oxidizing atmosphere [22].

16.5 Quality Specifications and Analysis

The quality of the cadmium depends on the production process. However, for 99.99%

cadmium, the following maximum impurity levels are generally accepted [11]: 1 ppm Cu, 5 ppm Pb, 5 ppm Tl, and 2 ppm Zn. For special purposes > 99.9998% cadmium is available.

The maximum amounts of impurities and the analysis procedures are given in ASTM C-752. Although the classical analytical methods for impurities are still used, today atomic absorption spectroscopy is the most common method [23].

16.6 Uses

Cadmium metal is used for cadmium coatings, nickel-cadmium batteries, and to a limited extent for reactor construction.

Electrodeposited Cadmium Coatings. Cadmium coatings are superior to other metallic coatings because of their optimal combination of properties: corrosion protection, ductility, frictional behavior, and soldering potential. Cadmium coatings have considerable significance in *automotive construction*, where disk brake calipers, bearing races, screws, nuts, bolts, springs, tubing connectors, contacts, and steering parts are all cadmium plated. In *machine construction and factory construction*, the surface of fastening elements, especially screws, is coated. Although the corrosion protection is most important, the frictional properties are also important. For example, even screws that are extremely tight must last for years and then be removable without difficulty. Precision screws and other connecting elements are subject to similar requirements. In the machines of chemical plants they are subjected to corrosion in addition. Aircraft parts not made from stainless steel are usually cadmium coated.

For the often necessary *attachment of different metals*, such as copper alloys, stainless steel, and titanium alloys to aluminum or magnesium alloys, cadmium coating is an absolute prerequisite to avoid corrosion. Cadmium plating is often required in military procurement contracts to ensure that the weapons and equipment function reliably over many years.

Nickel-Cadmium Accumulators. The second most widely used storage battery is based on cadmium and nickel. In the charged state the negative electrode consists of cadmium powder, and the positive electrode consists of nickel(III) hydroxide. As the battery discharges, cadmium hydroxide and nickel(II) hydroxide form. Charging reestablishes the original composition. The starting material for the production of the negative electrode is usually cadmium metal, which is dissolved in nitric acid and then precipitated as cadmium hydroxide. In another technique, cadmium hydroxide is repeatedly precipitated into the pores of sintered bodies, which become the negative electrode. A further variation uses electrodeposited cadmium powder, which is mixed with an electrical conductor such as graphite. A properly designed accumulating system does not release gas, even when overcharged, and can be sealed gastight. This development opened the way for new applications, such as rechargeable accumulators not larger than a single primary cell for use in portable electronic products.

In addition to the general advantages of accumulators, nickel-cadmium cells have a long life and are insensitive to low temperature and storage in the uncharged condition. Nonsealed nickel-cadmium accumulators are used in airplanes; telephone, telegraph, and radar stations; computer installations; and emergency power stations. Gastight cells are used in transportable pocket computers, razors, flashlights, etc.

Other Uses. Cadmium compounds, stabilizers for plastics, and pigments are generally produced from cadmium metal. The metal is dissolved in a mineral acid, usually sulfuric acid. Dissolution requires considerable time even at high temperatures. Increasingly, cadmium sheets from electrodeposition are used because they, unlike metal blocks, have a larger surface area and dissolve more quickly. Because they do not have to be melted, production costs are lower. In many cases, the high purity of the sheet allows direct use of the cadmium solution without additional purification,

especially as the noble impurities remain as residue.

Today a small amount of cadmium is converted into cadmium sulfide-copper sulfide *solar cells*, which directly convert light into electrical energy. The yield at present is $\approx 10\%$. A yield of 15% is thought to be attainable. It is expected that these cells can be produced inexpensively. Other cadmium compounds—cadmium telluride, cadmium selenide, and the combination cadmium sulfide-indium phosphide—have also been tested successfully. The amounts of cadmium consumed for the most important uses are given in Table 16.2.

16.7 Alloys

Numerous binary and tertiary cadmium alloys, often with complicated phase diagrams, are known. For practical purposes, cadmium does not dissolve in molten iron or aluminum. A tabular summary of cadmium alloys is available [24], and there is special literature about cadmium alloys [25]. A number of cadmium alloys, as a rule produced simply by melting, are used industrially. They can be divided by their principal use: solder, electrical conductors, and other.

Solder. Cadmium forms alloys with silver, copper, and zinc that have low melting points and are widely applicable for the hard soldering of metals. The cadmium lowers the melting point. More than 80% of the cadmium used in alloys is used for this purpose.

Aluminum or aluminum alloys can be soldered to copper, brass, or stainless steel by lead alloys that contain antimony, tin, and 2.6–17%, cadmium [26, 27]. Similar alloys that contain between 0.6 and 60% cadmium join glass and ceramics at temperatures under 180 °C [28]. For soldered connections on gold-plated electrical conductors, cadmium-containing zinc-lead-indium alloys are recommended [29, 30]. Occupational-medicine aspects of cadmium-containing soldering are treated in [31].

Electrical Contacts and Conducting Wire. The addition of cadmium or cadmium oxide to silver, often the contact material in electrical switches, reduces the metal loss due to sparking. In addition, the welding tendency is decreased. Cadmium (0.8–1%) improves the mechanical properties of copper wire without reducing its electrical conductivity. This is especially useful in the case of the overhead wires supplying power to electrically powered locomotives [32, 33].

Other Alloys. Cadmium is a component of a few bearing alloys based on tin, copper, and aluminum, usually in amounts under 1%. Wood's alloy and Lipowitz's alloy, which contain between 6 and 14% Cd, are used as fusible alloys in automatic fire-protection sprinklers and other devices. Cadmium in the form of a 5% alloy with silver and indium is put to use in the control rods of nuclear reactors because ^{113}Cd has a particularly large neutron capture cross section. A cadmium-selenium-indium alloy is an important component of a white-light laser for optical data processing systems [25].

16.8 Compounds

Generally water-soluble cadmium compounds are colorless. Aluminum and zinc can be used to precipitate cadmium metal from solutions of cadmium salts. From weakly acid or neutral solutions, cadmium sulfide is precipitated by hydrogen sulfide, sodium sulfide, and sodium hydrogensulfides. The temperature, concentration, and presence or absence of Cl^- determine the color of the precipitate: lemon yellow, orange, or even red. Sodium selenide precipitates black cadmium selenide. Mixed precipitates of cadmium sulfide and cadmium selenide are brown. Sodium hydroxide gives white cadmium hydroxide, which is insoluble in excess hydroxide. The precipitate formed by ammonia redissolves in excess reagent to form the complex $[\text{Cd}(\text{NH}_3)_6]^{2+}$. This complex also forms when ammonia is added to precipitates such as the hydroxide or oxalate. Sodium carbonate produces insoluble cadmium car-

bonate. Sodium cyanide reacts with aqueous cadmium solutions to give cadmium cyanide, which redissolves in excess reagent to form $[\text{Cd}(\text{CN})_4]^{2-}$. This complex is weak enough that the cadmium can be completely precipitated with hydrogen sulfide. Cadmium solutions react with hexacyanoferrate(II) to give a white precipitate, whereas they react with hexacyanoferrate(III) to give a yellow precipitate. Cadmium sulfite is only slightly soluble and can be precipitated from cadmium solution with sodium sulfite. All insoluble cadmium compounds can be dissolved in mineral acids. A few cadmium compounds fluoresce or phosphoresce, the silicate yellow to rose, the borate rose. Silver- or copper-activated cadmium-zinc sulfide gives colors spread over the entire spectrum.

The properties and uses of numerous cadmium compounds are described in [24]. The following text is limited to the most important industrial cadmium compounds.

Cadmium oxide, CdO . The amorphous form is yellow red, brown red, or brown black, the color depending on the particle size and the stoichiometry. It has a density of 6.95 g/cm^3 . The amorphous oxide is insoluble in water and bases but is readily soluble in dilute acids, ammonia, ammonium salt solutions, and sodium cyanide solutions.

The lustrous black cubic crystals of cadmium oxide have a density of 8.15 g/cm^3 . They sublime at $\approx 700^\circ\text{C}$. The low specific resistance at 0°C , $5.5 \times 10^{-3} \Omega\text{cm}$, is caused by an excess of Cd^{2+} ions, which makes CdO a semiconductor.

Cadmium oxide is produced by evaporation of cadmium metal and oxidation of the vapor. It can also be obtained by thermal decomposition of cadmium nitrate or carbonate or by oxidation of molten cadmium by an oxidizing agent. Commercial cadmium oxide should be completely soluble in sodium cyanide solution and contain no heavy-metal or sulfur impurities.

Cadmium oxide is used as a catalyst in oxidation-reduction reactions, dehydrogenation, cleavage, polymerization, the production of

multiply unsaturated alcohols, hydrogenation of unsaturated fatty acids, and as a mixed catalyst component to produce methanol from carbon monoxide and water. Further uses include resistant enamels, metal coatings for plastics, heat-resistant plastics, selenium ruby glass, starting material for other cadmium compounds, and stabilizers for poly(vinyl chloride). Cadmium oxide combined with an alkali-metal cyanide is the salt mixture used in the baths for cadmium electroplating. Cadmium oxide is a component of batteries. It is temperature resistant and together with silver useful in heavy-duty electrical contacts. Cadmium oxide improves the behavior of some high-temperature plastics.

Cadmium hydroxide, $\text{Cd}(\text{OH})_2$, is a colorless powder with a hexagonal, layered lattice. The precipitation of fine-grained cadmium hydroxide is only possible from nitric acid solution, basic salts often resulting from precipitation from other solutions. In the presence of halogenide ions, X^- , the complex $[\text{CdX}_4]^{2-}$ forms. In fact, precipitation of $\text{Cd}(\text{OH})_2$ can be prevented by a high concentration of alkali-metal chloride. Cadmium hydroxide is a component of cadmium nickel accumulators and silver-cadmium batteries. Cadmium hydroxide often replaces the oxide as the starting material for other cadmium compounds.

Cadmium carbonate, CdCO_3 , has a density of 5.3 g/cm^3 . (The density of $\text{CdCO}_3 \cdot \text{H}_2\text{O}$ is 4.3 g/cm^3 .) The white crystalline powder with an orthorhombic lattice of the calcite type decomposes above 360°C . Often precipitation with sodium carbonate produces hydroxy products, which contain water difficult to remove. Cadmium carbonate is a starting material for the production of cadmium pigments and other cadmium salts.

Cadmium chloride, CdCl_2 , has a density of 4.05 g/cm^3 . The colorless, lustrous orthorhombic crystals, which melt at 568°C to a liquid that boils at 967°C , are slightly soluble in water. The hydrates are $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$. Cadmium chloride

is produced by reaction of molten cadmium and chlorine gas at 600°C or by dissolving cadmium metal or the oxide in hydrochloric acid, subsequently vaporizing the solution. The salt is used in electroplating. An aqueous solution absorbs hydrogen sulfide. Molten cadmium chloride dissolves cadmium metal. Upon cooling, the metal precipitates.

The significance of cadmium chloride as a commercial product is declining. It occurs, however, as an intermediate in the production of cadmium-containing stabilizers and pigments, which are often obtained from a cadmium chloride solution itself obtained from cadmium metal, oxide, hydroxide, or carbonate.

Cadmium nitrate tetrahydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, has a density of 2.46 g/cm^3 . The small colorless deliquescent crystals readily dissolve in water. They have a *mp* of 59.9°C , and the liquid has a *bp* of 132°C . There are three hydrates, including the tetrahydrate, and the anhydrous salt (stability ranges):

$\text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$	(-16 to 3.5°C)
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	(3.5 to 48.7°C)
$\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	(48.7 to 56.8°C)
$\text{Cd}(\text{NO}_3)_2$	(> 56.8°C)

Cadmium nitrate is produced by dissolving cadmium metal in nitric acid, purifying if necessary, concentrating, and crystallizing. It is used for the production of red lusters in glass and porcelain and in cadmium-nickel sinter plates of storage batteries.

Cadmium sulfate, CdSO_4 , 4.7 g/cm^3 . The melting point of the anhydrous salt is 1000°C . Anhydrous cadmium sulfate is produced by melting cadmium with ammonium or sodium peroxodisulfate. A saturated aqueous solution contains 76 g CdSO_4 per 100 g of water at 0°C , 77.2 g at 20°C , 69.4 g at 74.5°C , and 58.0 g at 100°C .

$\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$, $\rho 3.09 \text{ g/cm}^3$. The colorless monoclinic crystals, which effloresce in air, are soluble in water (see above). This hydrate melts at 41.5°C in its own water of crystallization, converting to the monohydrate.

Calcium sulfate monohydrate, $\text{CdSO}_4 \cdot \text{H}_2\text{O}$, $\rho 3.79 \text{ g/cm}^3$, which is the form usually marketed, is produced by evaporating a cadmium sulfate solution above 41.5°C .

Cadmium sulfate is used in electroplating and as a starting material for pigments, stabilizers, and other cadmium compounds that can be precipitated from aqueous solution. It is used to produce fluorescent materials and in analysis. A cadmium sulfate solution is a component of the Weston cell, which has an almost constant voltage of 1.0186 V .

Cadmium cyanide, $\text{Cd}(\text{CN})_2$, $\rho 2.226 \text{ g/cm}^3$, is cubic and isostructural with $\text{Zn}(\text{CN})_2$. The solubility in water is 17 g per liter at 15°C . The solubility in sodium cyanide solution is greater because tricyanocadmium ions, $\text{Cd}(\text{CN})_3^-$ form. Cadmium cyanide is produced from dilute cyanic acid and cadmium hydroxide by evaporation or by precipitation from a concentrated solution of cadmium salt and alkali-metal cyanide. Cadmium cyanide and its mixtures with an alkali-metal cyanide are used in electroplating. Cadmium cyanide baths for the electroplating of cadmium metal coatings have the advantage that they are easy to work with. Metal removed from the solution as electroplate is replaced by dissolution of the cadmium anode. These cadmium anodes should be at least 99.95% pure.

Storage and Transportation. The labeling for transport of cadmium compounds in Germany and the European Economic Community are similar [34, 35]. The rules specify the use of certain symbols and directions for safety precautions. The international provisions for sea and air transport have recently been made compatible [36, 37], although special regulations for individual lands are often still very different. Frequently there are even different provisions for the various types of transportation or routes.

Table 16.1: Cadmium emission in Germany.

Source (Year)	Emission, t/a			
	Air	Soil	Water	Total ^a
Production of Cd metal and recycling (1980)	5-7	—	62	69
Pigments (1980)	0.17	—	1.2	1.4
Stabilizers (1980)	0.05	—	0.18	0.23
Electroplating (1981)	—	—	0.7	0.7
Batteries (1982)	0.31	—	0.9	1.2
Alloys (1982)	0.5	—	—	0.5
Glass (1982)	3	—	—	3
Fossil fuels (1982)	<5	—	—	5
Iron and steel (1982)	5	—	—	5
Cement (1982)	0.3	—	—	0.3
Fertilizer (1982)	—	35	0.5	35
Waste-water sludge (1982)	0.1	3.6-14.4 ^b	—	14
Man-made deposits (1982)	—	—	—	—
Waste burning (1982)	2.9-3.8	—	—	3.8
Automobile exhaust (1982)	<0.5	—	<0.5	1.0
Total, max.	26	49	66	140

^aMaximum.^bForty percent of the 1.8×10^{-6} t of waste-water sludge produced each year, or 0.72×10^{-6} t, is used agriculturally. If the sludge contains, on the average, 5 ppm Cd, this corresponds to the minimum estimate, 3.6 t Cd. Twenty ppm corresponds to the maximum estimate, 14.4 t Cd.

16.9 Environmental Protection

Cadmium has been ubiquitously distributed in the natural environment for millions of years, and information about this natural distribution in soil and water can be found in general literature, e.g., [24]. Industrial production of cadmium has affected the total distribution in soil and water only insignificantly, although in some restricted areas environmental problems have developed.

More than 90% of the total nonsmoker intake of cadmium is reported to be through food (see Section 16.11). All sources of cadmium that contaminate cultivated soil, whether by air, fertilizer, or water, should be reduced as much as possible.

Cases of cadmium poisoning caused by the contamination of the environment are described in Section 16.11.

16.9.1 Emission

Cadmium emission in Germany is given in Table 16.1. Summaries for the United Kingdom [38], the European Economic Community [39], and the United States [40] are difficult to compare because different parameters have been selected. However, this literature cites its sources, so comparison based on tabulations in these sources is possible. Data about industrial emission in the European Economic Community and extensive discussion of the technologies to reduce emissions have been collected [41].

16.9.2 Waste Water

Cadmium ions are normally separated from sewage by precipitation with an alkali-metal hydroxide or carbonate, with subsequent separation of the sediment. The required limit of 1 mg/L, however, is only attainable when the pH is adjusted to 9.5 or higher, and the precipitate is thoroughly separated from the solution. New regulations go even further and the "Cadmium Guidelines" for the European Economic Community require concentration limits of 0.3-0.5 mg/L after 1986 and <0.2 mg/L after 1989 [42]. These limits can only be met by manufacturers and consumers with special methods [41]. Especially useful for producers of cadmium and cadmium compounds are the coprecipitation of cadmium in so-called collectors and subsequent filtration or special treatment during production and before combination with cadmium-free waste water. In special cases, ion exchange, precipitation, for example, with a sulfide compound, or electrolytic separation is used. Clearly the most important factor is the reduction of the amount of cadmium carried into the waste water. Consequently the guidelines of the European Community concentrate on reduction of the amount of cadmium in waste water.

The constant tightening of the standards for waste water purification is intended to prevent excessive concentrations of cadmium in the sludge produced in biological waste-water treatment. When the concentration of heavy

metals is too high, the sludge can no longer be used in agriculture. In Germany, maximum cadmium content in sludge is restricted to 20 mg per kilogram of dry waste, along with a limitation on the total amount of waste [43]. Similar requirements are in preparation for the European Economic Community.

16.9.3 Air

Practically all cadmium emission sources are in the form of the oxide because this compound is formed in pyrometallurgical production, high-temperature processing, and combustion, either directly or via the metal. Initially the oxide is finely divided, but these fine particles can be made to agglomerate into coarse grains in suitable apparatus. However, this specialized apparatus is often not practical, and other methods, which also work well enough with fine particles, must be used. The laws vary from land to land. In *TA-Luft* (Technical Regulations for Air), a new proposal, Germany requires that not more than 0.2 mg Cd per m³ of air be released.

Larger gas effluents are usually subject to an electrostatic purification, for example, the removal of particles from gas exhausts of power plants and garbage disposal plants. For low cadmium contents this separation suffices. For high cadmium concentrations filtration is used. The filters can be made from metal screen, ceramic, or a variety of textiles. Regulations and gas release must be carefully adapted to conditions. Washing, especially with Demisters, has proved useful for removal of water-soluble aerosols [44].

16.9.4 Soil

Cadmium reaches agricultural soil via airborne particles; wastes, particularly sludge; and phosphate fertilizers. The importance of these three has been summarized and described for Germany [45].

The normal content of an agricultural field lies between 0.1 and 1 mg Cd per kilogram of soil (0.1-1 ppm). Maximum 3 ppm in a 30-cm layer of top soil is thought allowable, corre-

sponding to 13.5 kg/ha. The contribution to this reservoir per year is 7 g/ha from the air and 6 g/ha from phosphate fertilizer. The removal by harvest is about 4 g/ha. The annual increase is then 9 g/ha. This means that a soil with a content of 4.5 kg/ha, corresponding to 1 ppm, would reach the upper limit after 1000 years.

A number of studies deal with the disposal of sludge [46]. Even then there are still 265 years until the upper limit is reached; therefore, there is time to solve the problem of cadmium emissions. The national regulations for the production of waste-water sediment are tabulated in [47].

However, there are already problems associated with excessive cadmium contents in soil on the grounds of old mining and smelting plants. In the immediate vicinity of the sources of emission, the amount of cadmium in the soil exceeds that thought allowable. Here the use of the adjacent agricultural land must be limited, but there is no large-scale danger. Apparently man-made waste deposits do not create a cadmium source for plants since transfer of cadmium to the soil does not take place.

In addition to concern about the amounts of cadmium [48], the complicated mechanism of transfer from the soil to the plant must be considered. A transport model, from soil into the plant, has been proposed [39].

16.10 Economic Aspects

Since 1970 the production of the non-Communist countries has remained rather constant, 12-15 kt/a. The increase in European production was balanced by the decrease in North America. Consumption has remained in equilibrium with production. The amounts of cadmium for various uses have varied since 1970, affected by technical, economic, and environmental factors [49]. The cadmium price from 1970 to the beginning of the 1980s varied strongly, from \$0.50 to \$4 per pound. The consumption in the Western world between 1970 and 1982 is tabulated in Table 16.2. The figures are totals of the published statistics for

Germany, Japan, the United Kingdom, and the United States, which together account for about two thirds of non-Communist consumption.

Table 16.2: Consumption of cadmium, t.

Use	1970	1973	1976	1979	1982
Plating	3096	3273	3578	3326	2205
Batteries	680	1580	2106	2202	2180
Pigments	2021	3231	2466	2578	1819
Stabilizers	1947	1892	1195	1184	947
Alloys	642	877	519	400	488
Total	8386	10853	9864	9690	7639

16.11 Toxicology and Occupational Health

For more than a century there have been many reports on acute poisoning caused by cadmium compounds. Cadmium uptake occurred either via inhalation during occupational exposures or by oral poisoning due to ingestion of contaminated food or beverages [50]. About 35 years ago it was established [51] that long-term inhalation of cadmium oxide dust could cause a syndrome characterized by damage to the pulmonary and renal systems. Since then many studies have been made in various countries, establishing that occupational exposure to cadmium compounds can cause adverse effects, especially in the kidneys.

During the last decades it was also recognized that cadmium can cause renal effects in the general population. In Japan, a large population is exposed to cadmium via food, especially rice; in one area this resulted in an epidemic of chronic cadmium poisoning with severe bone damage, called *Itai-Itai disease*.

Whereas the exposure levels were reduced considerably in many industries, there is a growing concern about risks for the general population around the world. This is not only caused by emissions from industry. Waste disposal, especially by incineration, the increasing use of phosphate fertilizers, and pH changes in soil and water caused by acid rain are other factors of concern. For more detailed information on different aspects of occur-

rence, metabolism, and effects of cadmium, see [50, 52–56].

Exposure Levels. The average normal daily intake via food is 10–20 µg in most countries; considerably higher values, from 30 to above 200 µg/d, have been reported from certain areas in Japan [50, 52, 54, 55]. The highest cadmium concentrations are found in some basic foodstuffs such as wheat and rice and in liver, kidney, and certain seafoods. Drinking water generally is a minor source. Atmospheric levels of cadmium in rural areas are less than 1 ng/m³, in urban areas 1–10 ng/m³, and in certain industrialized areas a yearly average of up to 50 ng/m³ has been found [50]. Atmospheric exposure to cadmium therefore is of minor importance.

Tobacco may contain 1–2 µg Cd per gram, and smoking twenty cigarettes a day has been estimated to result in an inhalation of about 3 µg. Because a large part of that dose will be absorbed, exposure via cigarette smoking may contribute to the internal dose as much as that absorbed from food [50, 52, 55].

Metabolism. In order to understand the toxicity of cadmium some basic facts about the metabolism of this metal must be known.

The fate of inhaled cadmium compounds depends on particle size and solubility. Finely divided cadmium oxides, especially fumes, deposit in the lower respiratory tract, because of their relatively high solubility about 30% of the inhaled amount is absorbed. Cadmium sulfide and sulfoselenide are relatively slightly soluble, and they are not absorbed to the same extent. (Mucociliary transport to the gut occurs, but the absorption from the gut probably is only a few percent.)

Ingested cadmium generally is absorbed to a few percent [50, 57]. Nutritional deficiencies, e.g., in iron and calcium, will cause higher absorption. Women with severe iron depletion absorbed up to 20% of the cadmium ingested orally [57].

Cadmium absorbed from the lungs or the gut initially is stored mainly in the liver. Exposure to cadmium induces the synthesis of metallothionein, a low molecular mass, cysteine-

rich protein, which strongly binds cadmium but also zinc and copper [58]. The liver has a high capacity to synthesize this protein, and even at very high exposures most of the cadmium in the liver will be bound to metallothionein. The protein breaks down relatively fast, but continuous synthesis ensures that cadmium does not escape to bind to other structures.

In the blood, cadmium is found in the cells and plasma, the concentrations being approximately equal. However, with increasing cadmium levels in the body more cadmium will be found in the cells. In the red blood cells cadmium is bound to several proteins, a major part to metallothionein. In plasma only a minor part is bound to metallothionein. Plasma metallothionein easily passes the glomeruli, and as a protein it will be reabsorbed in the proximal tubules. In the kidneys the protein then breaks down, and cadmium is released. The kidney can also synthesize metallothionein, which ensures that cadmium is trapped in an inert form. However, when the synthesizing capacity is exceeded, cadmium ions will be released and toxic effects may occur.

The cadmium excretion from the kidney is very small. Long retention times in liver and kidney, as well as in other tissue, lead to an accumulation of cadmium in the kidneys from birth to middle age. The newborn is virtually free from cadmium because the placenta is an efficient barrier. The gross biological half-life of cadmium in the body has been estimated to be about twenty years [50].

The average cadmium concentration in the liver of adults is about 1 mg/kg wet weight; the concentration in the renal cortex is about 20 mg/kg in most European countries and in North America [55, 56, 59]. In Belgium higher concentrations, on the average 40 mg/kg in renal cortex, have been reported [60]. The highest concentrations in members of the general population have been found in Japan [55, 58, 59, 60].

Smokers generally have about twice as high cadmium concentrations in the renal cortex (about 25 mg/kg wet weight) as compared with nonsmokers [59, 60].

In the blood the cadmium concentrations in nonsmokers are generally less than 1 µg/L, whereas smokers have up to 5 µg/L [60]. The difference between smokers and nonsmokers is also obvious in the urine. Nonsmokers in Europe and North America excrete about 0.4 µg/g creatinine, whereas smokers excrete about twice as much [59, 61]. This urinary excretion is related to the level of cadmium in the body and is useful for monitoring general populations as well as most persons that are occupationally exposed to cadmium. The total body burden in adult nonsmokers generally is less than 10 mg [59], whereas that of the newborn is only a few micrograms.

Acute Toxicity. Acute cadmium poisoning by inhalation has mainly been caused by accidental exposure to cadmium fumes. The highest risk is in welding, cutting, or soldering operations when cadmium-containing materials are treated, especially if the worker is unaware cadmium is present. There may be a latent period of up to 24 h after exposure before symptoms occur. Chemical pneumonitis occurs, which may lead to lung edema and general symptoms, in some cases with lethal outcome [50, 55, 62, 63].

The concentration of cadmium in the air has not been measured at the time of accidents. Based on cadmium analysis of lung tissue from people dying after acute exposure it has been estimated that the lethal dose corresponds to 1 mg/m³ as cadmium fume for eight hours. Concentrations of 0.5–1 mg Cd/m³ for a couple of hours may cause pneumonitis [53]. A short-term exposure limit for cadmium oxide fumes and respirable dust of 0.25 mg Cd/m³ has been recommended to prevent acute lung reactions [53].

Single oral doses of about 10–15 mg may cause gastrointestinal disturbances, but the lethal dose is probably several hundreds of milligrams [53, 55].

Chronic Toxicity. The chronic effects after long-term inhalation are mainly seen in lungs and kidneys [50, 51, 55]. In earlier times anemia, anosmia, and yellow lines on the teeth were common among cadmium workers but

are uncommon today. Emphysema was a major finding in some earlier studies involving exposure to cadmium oxide fume and dust [50]. Because of the decrease in exposure, lung dysfunction is nowadays rare, and if it occurs the symptoms are mild. Figure 16.2 shows how air concentrations of cadmium have decreased during the years in a Swedish factory, where emphysema was seen in the 1940s [51, 64]. It has been concluded that to prevent any pulmonary effect of cadmium the time-weighted average concentration of respirable dust in air should not exceed $20 \mu\text{g}/\text{m}^3$ [53].

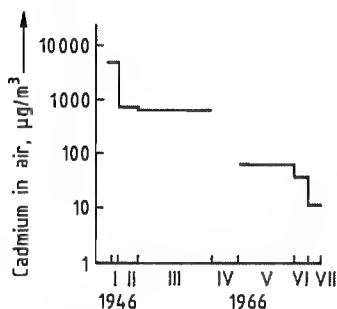


Figure 16.2: Concentration of cadmium in workroom air from 1946 to 1977. Arithmetic means of personal and stationary samples were obtained within seven subperiods. Data covering period IV, 1961–1964, are not available.

The critical effect of cadmium is *renal tubular dysfunction*. In 1950 it was discovered that workers exposed to cadmium oxide dust in an alkaline battery factory had an unusual type of proteinuria [51]. The majority of the proteins were of low molecular mass. Studies of renal function showed that the glomerular filtration rate and the concentrating capacity were decreased. The proteinuria in chronic cadmium poisoning is a tubular proteinuria, caused by a decrease in the reabsorption of filtered plasma proteins in the proximal tubules [50].

The urinary excretion of protein was found to be related to exposure time [65]. The critical cadmium concentration in renal cortex was estimated to be 200 mg/kg wet weight [50]. This value was confirmed by further studies [66–68] and is to be compared with the normal concentrations reported in the previous sec-

tion. A critical urine concentration of about $10 \mu\text{g}$ of cadmium per gram of creatinine has also been established, which generally is a good indicator of the body burden [50, 67–69].

The best dose-response relationship seems to be between cadmium concentration in the liver, determined by *in vivo* neutron activation, and the degree of tubular dysfunction [67]. At liver concentrations above 30 mg/kg wet weight proteinuria appeared; this corresponds to a cadmium concentration in renal cortex of about 200 mg/kg .

At present, the increased excretion of low molecular mass proteins is regarded as the first sign of renal tubular effects caused by cadmium. This is also consistent with the fact that cadmium primarily is deposited in the proximal tubules, because the cadmium-containing metallothionein is reabsorbed.

At this early stage there are no measurable changes in the excretion of other substances. However, if exposure goes on and the renal levels increase, other functions may be disturbed. In advanced cases of chronic cadmium poisoning the excretion of glucose, amino acids, and phosphate is increased (Fanconi syndrome). Disturbances in mineral metabolism may cause the formation of renal stones. For detailed discussion, see [70, 71].

The *diagnosis* of chronic cadmium poisoning must be based on occupational history, exposure levels in air, levels of cadmium in blood and urine, and protein analysis in urine.

The tubular damage is irreversible, and *prevention* is thus more important than diagnosis. The determination of cadmium in whole blood gives information about recent exposure, but is not always a good indicator of the body burden or risk for renal dysfunction, especially in smokers. Cadmium in urine should be used to monitor this risk. As long as the urinary excretion of cadmium is below $5 \mu\text{g}$ per gram of creatinine there should be no risk for the kidneys. At concentrations of $5\text{--}10 \mu\text{g}$ per gram of creatinine, exposure should be minimized to prevent further accumulation in the kidneys.

Monitoring is also necessary after exposure has ceased. Intensive exposure during rela-

tively short periods may lead to a high cadmium concentration in the liver. Cadmium will then be released from the liver and transported to the kidneys for a long time. The renal concentrations may reach a critical level many years after the last exposure.

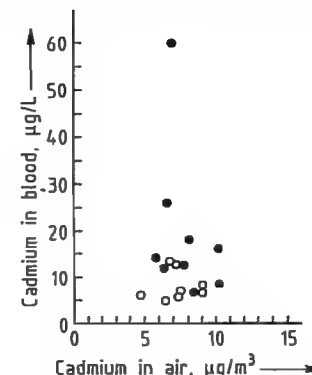


Figure 16.3: Cadmium in blood vs. cadmium in air. Arithmetic means of 4–5 samples of blood cadmium and 9–11 personal samples of airborne cadmium dust for 17 alkaline battery workers. Smokers are represented by the solid circles; nonsmokers, by open circles.

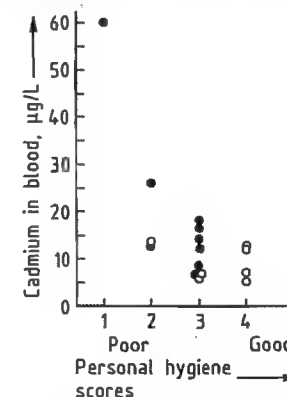


Figure 16.4: Cadmium in blood in relation to the personal hygiene score. Arithmetic means of five samples of cadmium in blood from nine smokers (solid circles) and of 4–5 samples from nine nonsmokers (open circles).

The concentration of cadmium in air is seldom of help in evaluating risks. The long biological half-life of cadmium will lead to a continuous increase in renal levels over many years, and past exposure often is more important than present exposure. Changes in workplace exposure during several decades are shown in Figure 16.2. Figure 16.3 demon-

strates that cadmium blood levels vary greatly even at the current low exposure levels. This is most obvious with smokers. The natural cadmium content of cigarettes does not explain this finding, which is caused instead by contamination of cigarettes or pipe tobacco during work and poor personal hygiene, as illustrated in Figure 16.4 [63].

Therefore, it is imperative to prevent smoking in the workshops and the carrying of tobacco in work clothes; such measures will have much more impact than small reductions of cadmium concentrations in air. Dust accumulation must be prevented in the workshop to minimize exposure caused by contamination of work clothes and hand-to-mouth transfer. The latter may lead to considerable gastrointestinal exposure [72].

The present threshold limits for cadmium in air differ among countries, varying from $10 \mu\text{g Cd}/\text{m}^3$ in Finland to $100 \mu\text{g}/\text{m}^3$ (total dust) in East European countries. The low values, $10\text{--}20 \mu\text{g}/\text{m}^3$, should prevent renal damage, but as indicated above, smoking and poor personal hygiene may increase the internal exposure.

Carcinogenicity. Cadmium has been implicated as a carcinogenic agent, especially with regard to cancer of the prostate. The evidence is weak and based on deaths from cancer of the prostate. However, this cancer is extremely common among elderly men, and it often does not give any symptoms [73, 74]. There is therefore no evidence that cadmium induces this cancer; diet and hormonal factors are more important determinants. However, it cannot be excluded that in heavily exposed workers cadmium might have affected zinc metabolism in the prostate or caused hormonal changes. It is extremely unlikely that low exposures will have any effect on the prostatic function.

According to animal experiments long-term exposure to cadmium chloride aerosols causes lung cancer in rats [75]. The concentrations of cadmium in air were relatively low, $12.5\text{--}50 \mu\text{g}/\text{m}^3$, but exposures were for 23 h a day. Humans are generally not exposed to cad-

mium chloride. In Germany cadmium chloride has been listed as a carcinogen. There have been a number of studies on the occurrence of lung cancer among workers exposed to cadmium oxide dust, but there are no conclusive results indicating that cadmium oxide causes lung cancer in humans [73].

Poisoning from Contamination of the General Environment. Contamination of the general environment has caused cadmium poisoning in certain areas of Japan [64]. Cadmium levels in rice caused daily intakes of several hundreds of micrograms, which should be compared to the "normal" intake of 10–20 μg in most countries in Europe and North America. The exposure in Japan has caused renal tubular dysfunction of the same type as described in the section on chronic toxicity. In one area in the Toyama prefecture the cadmium exposure resulted in the development of severe bone damage, Itai-Itai disease. Mainly multiparous women above 40 years of age were affected. The males in the area had tubular dysfunction but generally did not develop the bone disease. The women had poor nutritional status with deficient intakes of calcium, vitamin D, and protein, probably also of iron. Cadmium alone can hardly cause such severe bone changes, but combined with severe calcium deficiency the result became disastrous. It is not likely that Itai-Itai disease will occur again, but as mentioned tubular dysfunction is common in several other areas of Japan.

There are some contaminated areas in Europe, where signs of renal disease have been sought [76, 77]. No definite conclusions can yet be drawn, but the investigated populations had higher cadmium levels than generally found in Europe [77, 78].

Most domestic animals are not at risk for cadmium poisoning. An exception is the horse. Adult horses generally have about five times higher cadmium concentrations in the renal cortex than adult humans in the same area [79].

16.12 Cadmium Pigments

Among the inorganic pigments, cadmium pigments have particularly brilliant red and yellow colors, as well as a high durability. All cadmium pigments are based on cadmium sulfide and crystallize with a hexagonal wurtzite lattice (Figure 16.5). The sulfur atoms have a hexagonal, tightly packed arrangement, in which the cadmium atoms occupy half of the tetrahedral holes. In this wurtzite lattice the cations and anions can be replaced within certain limits by chemically similar elements; nevertheless, the only substitutions which are used in practice are zinc and mercury for the cations and selenium for the anions.

The use of zinc yields greenish yellow pigments due to the lower lattice constants; mercury and selenium lead to expansion of the lattice. With an increasing content of selenium, or especially mercury, the shades of the pigments change to orange, red, and ultimately to deep red (bordeaux). The brilliant colors of cadmium pigments are primarily due to their almost ideal reflectance curves with a steep ascent (Figure 16.6).

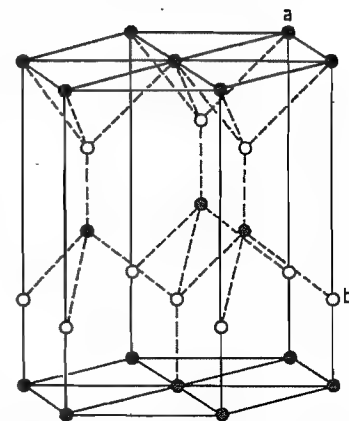


Figure 16.5: Crystal lattice of cadmium pigments (wurtzite structure): a) Sulfur (selenium); b) Cadmium (zinc, mercury).

16.12.1 Cadmium Sulfide

Cadmium sulfide, CdS , occurs as greenockite or cadmiumblende in several natural deposits, which are, however, of no importance

as pigments. The mineral crystallizes hexagonally in the wurtzite lattice (α -form).

When hydrogen sulfide is passed into cadmium salt solutions, cadmium sulfide is formed as a yellow precipitate with a zinc blende structure (cubic, β -form). The β -form can be converted into the α -form (e.g., by heating). α -Cadmium sulfide shows photoconductivity due to defects in the crystal lattice (usage in photovoltaic cells) [80]. The solubility in water at 25 $^{\circ}\text{C}$ is 1.46×10^{-10} mol/L [81]. Cadmium sulfide forms the basis for all cadmium pigments.

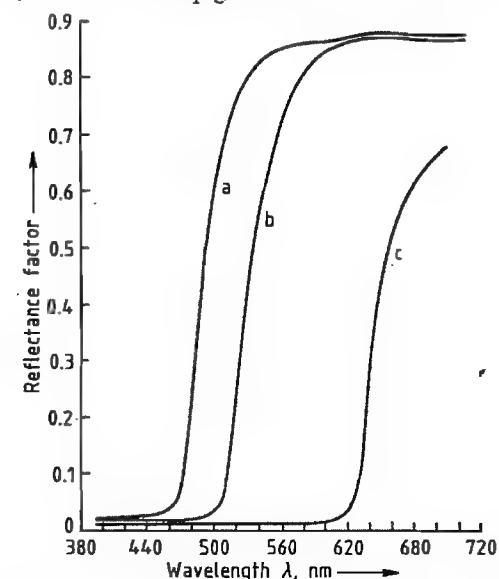


Figure 16.6: Reflectance curves of cadmium pigments (pigment volume concentration 10%): a) Cadmium yellow; b) Cadmium golden yellow; c) Cadmium red (bordeaux).

16.12.2 Cadmium Yellow

Cadmium yellow consists of pure cadmium sulfide (golden yellow color) or mixed crystals of zinc and cadmium sulfide, $(\text{Cd}, \text{Zn})\text{S}$, in which up to one-third of the cadmium can be replaced by zinc. The density of this pigment is 4.5–4.8 g/cm^3 and its refractive index is 2.4–2.5. The prevalent particle size is ca. 0.2 μm with cubic to spheroidal habits. Cadmium yellow is practically insoluble in water and alkali, and of low solubility in dilute mineral

acid. It dissolves in concentrated mineral acid with generation of hydrogen sulfide.

Production. The raw material for the production of cadmium yellow pigments is high-purity cadmium metal (99.99%), cadmium oxide, or cadmium carbonate. If the metal is used it is first dissolved in mineral acid. A zinc salt is then added to the solution; the amount added depends on the desired shade. The zinc salt is followed by addition of sodium sulfide solution. An extremely finely divided cadmium sulfide or cadmium zinc sulfide precipitate is formed, which does not possess any pigment properties. This intermediate product can also be obtained by mixing the cadmium or cadmium-zinc salt solution with sodium carbonate solution. An alkaline cadmium carbonate or cadmium zinc carbonate precipitate is formed which reacts in suspension with added sodium sulfide solution.

The crude precipitated cadmium yellow is washed and then calcined at ca. 600 $^{\circ}\text{C}$, at which temperature the cubic crystal form changes to the hexagonal form. This process determines the particle size distribution, which is essential for the pigment properties.

If the starting material is cadmium oxide or cadmium carbonate, it is mixed with sulfur and calcined at ca. 600 $^{\circ}\text{C}$. After calcination, the pigment product is washed with dilute mineral acid to remove any remaining soluble salts, dried, and ground.

16.12.3 Cadmium Sulfoselenide (Cadmium Red)

Pure cadmium selenide, CdSe , is brownish black and has no pigment properties. Like cadmium sulfide, it is dimorphous and occurs in hexagonal and cubic modifications. Cadmium selenide is insoluble in dilute acid. It readily liberates hydrogen selenide in concentrated hydrochloric acid. It dissolves completely in fuming nitric acid, the Se^{2-} ions being converted to SeO_4^{2-} ions. Cadmium selenide is an n-type semiconductor.

Cadmium red consists of cadmium sulfoselenide, $\text{Cd}(\text{S}, \text{Se})$, and is formed when sulfur

is replaced by selenium in the cadmium sulfide lattice. With increasing selenium content, the color changes to orange, red, and finally dark red. The density of these pigments increases correspondingly from 4.6 to 5.6 g/cm³ and the refractive index from 2.5 to 2.8. The crystals have cubic or spheroidal habits, the prevalent particle size is 0.3–0.4 µm.

Production. Cadmium red pigments are produced in a similar way to the cadmium yellow pigments. The cadmium salt solution is prepared by dissolving the metal in mineral acid and then sodium sulfide is added. A certain amount of selenium powder is dissolved in the sodium sulfide solution to obtain the desired color shade. In an alternative procedure, the cadmium solution is mixed with sodium carbonate solution to precipitate cadmium carbonate which is reacted with the selenium-containing sodium sulfide solution.

The cadmium red pigment intermediate is obtained as a precipitate which is filtered off, washed, and calcined at ca. 600 °C. As with cadmium yellow, calcination yields the red pigment and determines the particle size, particle size distribution, and color shade. Analogously to the cadmium yellow process, cadmium red can be produced by direct reaction of cadmium oxide or cadmium carbonate with sulfur and the required amount of selenium at ca. 600 °C.

Products in which selenium is totally or partially replaced by tellurium [82, 83] have not had any commercial application owing to their poor coloristic properties.

16.12.4 Cadmium Mercury Sulfide

The cadmium in the wurtzite lattice of cadmium sulfide can be replaced by divalent mercury to give cadmium mercury sulfide (cadmium cinnabar). As the quantity of mercury increases, the lattice expands, and the color deepens, changing from yellow to orange and finally dark red. The coloring properties of cadmium cinnabar resemble those of the selenium-containing cadmium red pig-

ments. Use of these mercury-containing pigments can be justified for economic reasons. However, their use is no longer justifiable from the ecological point of view because adequate nontoxic substitutes are available.

16.12.5 Properties and Uses

Cadmium pigments are mainly used to color plastics. They have brilliant, pure shades (yellow, orange, red, and bordeaux), good hiding power, and moderate tinting strength.

Their process-relevant properties are determined by their high thermal stability and chemical resistance to aggressive additives or to molten plastics that have a reducing action (e.g., polyamides). Other advantages for use in plastics are good lightfastness, weather resistance, and migration resistance. The cadmium pigments also protect polyalkenes against aging because they absorb UV light. Premature embrittlement is prevented and the polymer can be recycled [84].

A very useful feature of plastics colored with cadmium pigments is the dimensional stability of injection-molded parts with a large surface area. The combination of these properties is not matched by any other class of colorant.

For economic reasons, cadmium pigments are no longer used for coloring plastics where the pigment property requirements are less stringent. In poly(vinyl chloride) and to a large extent in low-density polyethylene, they have been replaced by less expensive inorganic and organic pigments.

For ecological reasons, cadmium pigments are increasingly being replaced in plastics where high demands are made on the colorants, sometimes with concessions as regards product quality. Plastics processed at high temperature are now colored with high-quality organic pigments (e.g., perylene, quinacridone, and high-quality azo pigments). On account of the color stability of the cadmium pigments at high temperatures, there are very few alternatives for the following applications in the plastic industry:

- Processing temperatures above 300 °C

- Aggressive plastic melts
- Outdoor uses

A further use of cadmium pigments is in paints and coatings (powder paints, silicone resins, and automotive topcoats) but this is declining.

Cadmium pigments are irreplaceable for coloring enamels, ceramic glazes, and glass. Brilliant transparent glasses are obtained by adding a small amount of cadmium red, while 10% cadmium red with a cadmium oxide stabilizer produces dark decorative glasses. Other areas of application are ceramics (wall and floor tiles, household and decorative ceramic ware). Very small amounts of cadmium pigments are used for artists' colors. The terms cadmium yellow and cadmium red have become synonyms for very brilliant red and yellow shades.

Cadmium pigments, especially cadmium red, are very sensitive to intensive grinding, which causes loss of brilliance due to an increase in the number of irregular lattice defects. A brilliant red shade may become a dirty brownish red.

The cadmium pigments are lightfast but, like all sulfide pigments, are slowly oxidized to soluble sulfates by UV light, air, and water. This photooxidation is more pronounced with cadmium yellow than with cadmium red and can still be detected in the powder pigment which normally contains 0.1% moisture.

16.12.6 Quality Specifications

The quality requirements and conditions for the supply of cadmium pigments given in ISO 4620 have lost their significance in practice. According to this standard, cadmium pigments must be free from organic colorants, inorganic colored pigments, and other additives. The acid-soluble components (0.1 mol/L HCl) should not exceed 0.2% Cd (determined according to ISO 4620 and ISO 3856/4); in practice, they are usually < 0.01% Cd.

Cadmium pigments are sold as homogeneous powders and as preparations mixed with barium sulfate to give the required tinting

strength. To reduce the risk of inhalation, they are supplied as low-dust powders and fine granules.

In dust-free and dispersed form, they are supplied as concentrated plastic granules (master-batch pellets), as concentrated pastes, and as liquid colors. These products are added at different stages in the processing of plastics.

16.12.7 Economic Aspects

The output of cadmium pigments in the industrialized countries in 1990 was ca. 5800 t, of which 2800 t were produced in Europe and 2000 t in the United States. Consumption is distributed approximately as follows: plastics 90%, ceramics 5%, and others 5%.

Manufacturers and trade names of cadmium pigments include BASF Lacke + Farben, Stuttgart, Germany (Sicotherm Pigments); Degussa, Frankfurt, Germany; Orkem, Narbonne, France (Langdopec Pigments); Blythe Colours, Stoke on Trent, UK; Brown, London, UK; Reckitts, Hull, UK; Ferro Corporation, Color Division, Cleveland, USA; and Harshaw Chemical Co., Cleveland, USA.

16.12.8 Toxicology and Environmental Protection

Production. Since soluble cadmium compounds have a toxic effect on humans and the environment, all wastewater originating from the production of cadmium pigments must be treated to remove cadmium. This is carried out by methods outlined elsewhere. In the EC, the following limits for the pigment production must be observed: 0.2 mg Cd/L in wastewater and 0.3 kg Cd per tonne of used cadmium compounds calculated as metal [85].

The exhaust air from the production plants and the ventilation equipment must be cleaned. Tubular filters and, more recently, absolute filters have been used to remove cadmium compounds in dust form. With these high-performance filters, it is possible to comply with the limits specified in Germany (0.2 mg Cd/m³ air, 1 g Cd/h, emission limit; 5 µg

Cd/m² per day, immission limit). During pigment production, occupational hygiene and safety measures for toxic materials must be observed. Exposure to cadmium can be determined by measurements of the workplace concentration and by examination of the cadmium levels in blood and urine. In Germany, the following maximum biological tolerance levels are allowed at the workplace (BAT values): 15 µg Cd/L urine and 1.5 µg Cd/100 mL blood. In the future, a TRK value will apply which is below the earlier MAK value of 50 µg Cd/m³. In the United States, the TLV value for cadmium fumes and salts is 50 µg Cd/m³. Lower values have been recommended by OSHA, but they are still being discussed.

Toxicity. The toxicity of soluble cadmium compounds is described elsewhere. Cadmium pigments are cadmium compounds with a low solubility, however, small quantities of cadmium dissolve in dilute hydrochloric acid (concentration equivalent to stomach acid), and in cases of long-term oral intake of cadmium pigments, they can accumulate in the human body. On inhalation of subchronic amounts of cadmium pigments, a small proportion of cadmium is biologically available [86, 87].

Cadmium pigments have no acute toxic effect (oral LD₅₀, rat, > 10 g/kg). The pigments do not have any adverse effects on the skin and mucous membranes.

Genotoxic Effects and Carcinogenicity. Tests for damages of the DNA [88] and cell transformation caused by crystalline cadmium sulfide were positive [89]. Cadmium sulfide also proved to be carcinogenic by intraperitoneal and after intratracheal administration [90]. The significance of such animal studies is being controversially discussed by toxicologists.

Long-term animal feeding studies with various cadmium compounds show no carcinogenic risks. However inhalation studies with rats, mice, and hamsters (with cadmium chloride, cadmium sulfate, cadmium chloride, and cadmium sulfide) showed that all four compounds produced a significant increase of lung

cancer in rats [91]. The results for mice were inconclusive and no carcinogenicity in hamsters was observed [92]. Reinvestigation of the inhalation studies has shown that the test was not applicable to cadmium sulfide. The inhaled liquid cadmium sulfide suspension contained ≤ 40% cadmium sulfate formed by light-induced oxidation.

In 1989 the German Senate Commission for the Assessment of Dangerous Substances classified cadmium and its compounds (including cadmium sulfide) as substances that have carcinogenic properties as found in animal studies. Cadmium pigments and preparations which contain cadmium pigments in concentrations above 0.1%, must therefore be regarded as carcinogenic if they occur in an inhalable form.

In the United States, the National Toxicology Program (NTP) has shown that cadmium and different cadmium compounds (including cadmium sulfide) have a carcinogenic effect in animal experiments.

In 1991 the EC reported the above-mentioned fault in the inhalation studies and classified cadmium sulfide in the EC Cancer List in Category III (suspected carcinogen).

Limitations of Use. In 1981 Sweden prohibited the use of cadmium pigments (with some exceptions) for ecological reasons. In 1987 Switzerland prohibited the use of cadmium pigments in plastics. Exceptions are possible if valid reasons can be given.

In 1991 the EC passed a directive to prohibit the use of cadmium pigments as colorants for certain plastics that can easily be colored with other pigments [93]. For further series of plastics, use of substitution pigments will be compulsory in 1996. Plastics that require high processing temperatures or that are mainly for outdoor use are not affected by this prohibition owing to the poor performance of possible substitution pigments.

In 1996 the use in coating media will be prohibited. Use in artists' colors and ceramic products is still permitted.

Regulations Affecting Foods. The cadmium pigments fulfill the legal requirements of the

EC countries for colorants used in plastics which come in contact with food. Except for polyamide 6, only microgram quantities of cadmium can be extracted from colored plastics into simulants [94, 95].

To prevent even minimal intake of cadmium, the European Commission has passed a resolution which states that cadmium pigments should only be used for these purposes if adequate substitutes are not available [96].

The use of cadmium pigments in ceramics is controlled in the EC Guideline No. 84/500/EC. International standards [Part I (Methods) and Part II (Limit Values)] are as follows: ceramic surfaces ISO 6486, enamel ISO 4531, and glass ISO 7086.

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17 Mercury

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17.1 Introduction

Mercury (also called quicksilver), symbol Hg from the Greek υδραρ = water and αργυρος = silver, was known as early as 1000 B.C. because of its liquid state at room temperature ($mp -38.89^\circ\text{C}$). The discovery in 1938 of 1 kg of the metal in 2500-year-old sand layers on the eastern coast of Greece indicates that mercury was used in the extraction of gold at an early date [1]. Mercury was mentioned about 200 B.C. in India as well as in China (Han dynasty).

As early as 1556, GEORGES BAUER, known as AGRICOLA, reported five different methods for extracting mercury from its ores [2]. He also realized that mercury vapors are heavier than air and that they could therefore conveniently be trapped in condensers beneath the reaction vessel.

Because of the considerable vapor pressure of mercury even at room temperature and the toxicity of its vapors, particularly safe and reliable methods must be used in the extraction of mercury to avoid releasing even the slightest trace of the metal into the environment. The problem of gas and water purification is therefore particularly important.

17.2 Properties

17.2.1 Physical Properties

Mercury is a silvery-white, shiny metal, which is liquid at room temperature. The most important physical properties are listed below:

Isotope masses (ordered according to decreasing abundance)	202, 200, 199, 201
mp	-38.89°C
bp (101.3 kPa)	357.3°C
Density (0°C)	13.5956 g/cm^3
Specific heat capacity c_p (0°C)	$0.1397\text{ J g}^{-1}\text{K}^{-1}$

Heat of fusion	11.807 J/g
Heat of evaporation (357.3 °C)	59.453 kJ/mol
Thermal conductivity (17 °C)	0.082 Wcm ⁻¹ K ⁻¹
Thermal expansion coefficient β (0–100 °C)	1.826×10^{-4} K ⁻¹
Electrical conductivity (0 °C)	1.063×10^{-4} m Ω^{-1} mm ⁻²
Crystal structure	rhombohedral
Viscosity (0 °C)	1.685 mPa·s
Surface tension	480.3×10^{-5} N/cm
t_{crit}	1450 °C
p_{crit}	105.5 MPa
Critical density	5 g/cm ³
Evaporation number (25 °C)	0.085 mgK ⁻¹ cm ⁻²

Mercury has a relatively high vapor pressure, even at room temperature. Saturation vapor pressures at 0–100 °C are listed in Table 17.1 (corresponding to a specified mercury content in air). The temperature dependence of the density of mercury is given in Table 17.2.

Mercury vapor is excited to a state of luminescence by electrical discharge (mercury vapor lamps). Ultraviolet radiation is released primarily, it can be used to start and to promote chemical reactions.

Table 17.1: Saturation vapor pressure of mercury at different temperatures.

t , °C	p , Pa	Hg content in air, g/m ³
0	0.026	0.00238
10	0.070	0.00604
20	0.170	0.01406
30	0.390	0.03144
100	36.841	2.40400

Table 17.2: Density of mercury as a function of temperature.

t , °C	Density, g/cm ³	t , °C	Density, g/cm ³
-38.89	13.6902	200	13.1139
0	13.5956	250	12.9957
50	13.4733	300	12.8778
100	13.3524	350	12.7640
150	13.2327		

Table 17.3: Temperature dependence of the dynamic viscosity of mercury.

t , °C	Density, g/cm ³	t , °C	Density, g/cm ³
-20	1.855	60	1.367
-10	1.764	80	1.298
0	1.685	100	1.240
10	1.615	200	1.052
20	1.554	300	0.950
30	1.499	340	0.921
40	1.450		

The surface tension of mercury is ca. six times greater than that of water, which is the reason for its poor wettability by water.

The dynamic viscosity η of mercury (Table 17.3) is of the same order of magnitude as that of water [3].

Some other metals, such as gold, silver, and zinc, dissolve readily in mercury to form amalgams. The solubility of mercury in water is strongly temperature dependent [4]. At room temperature, the solubility is ca. 60 μ g/L; at 50 °C, ca. 250 μ g/L; and at 90 °C, ca. 1100 μ g/L. At low temperature, the addition of sodium chloride reduces the water solubility.

17.2.2 Chemical Properties

Mercury exists in the oxidation states 0, 1+, and 2+; monovalent mercury is found only in Hg–Hg bonds. The redox potentials E^0 at 298.15 K and 101.325 kPa relative to the standard hydrogen electrode are as follows [3]:



The standard potentials show that mercury is a relatively noble metal. Metallic mercury dissolves in nitric acid, aqua regia, warm concentrated hydrochloric acid and sulfuric acid. It is sparingly soluble in dilute HCl, HBr, and HI as well as in cold sulfuric acid. Most of its chemical compounds have densities of 5–9 g/cm³. The oxide of mercury (HgO) decomposes at 400–500 °C. This effect is utilized in the extraction of mercury from oxidic sources. Mercury forms monovalent and divalent compounds with the halogens fluorine, chlorine, bromine, and iodine. It also forms monovalent and divalent compounds with sulfur.

17.3 Resources and Raw Materials

17.3.1 Deposits

All known mercury ores are relatively low-grade ores, the average mercury content being ca. 1 %. Because mercury ores lie close to the earth's surface, the mining depth is ca. 800 m at most. The overwhelming proportion of mercury has always been produced in Europe; some of the most important deposits are listed below. Over the last ten years, the former Soviet Union, Spain, China, Algeria, Turkey, and the United States have accounted for ca. 90 % of world mining production.

Spain. The deposits at Almadén have been mined for more than 2000 years. Almadén is situated in the southwest of the province of Ciudad Real in New Castile, about 200 km from Madrid, on the northern edge of the Sierra Morena. The ore-bearing deposits are porous sedimentary rocks (sandstone, bituminous shale, Silurian quartzite) that contain mercury sulfide (cinnabar). Needles of coarsely crystalline cinnabar as well as metallic mercury in lenticular ore-bearing bodies are also found over a roughly 20-km stretch in the valley of the Valdeazogues river. The ore is extracted in several mines (San Pedro y San Diego, San Francisco, San Nicolas). The richest strata contained 12–14 % mercury at a depth of 170–200 m. Mining is carried out today at a depth of 500 m; 1 t of ore yields about one flask of mercury (= 34.473 kg of mercury, corresponding to a 3.5 % mercury content in the ore).

This deposit was probably known to the Celts and Phoenicians, and was mined by the Romans from 150 B.C. These mines were subsequently worked by the Moors, then by the orders of knights, by the Spanish royal house, and from 1525–1645 by the Fuggers. Since then the mines have been under state management. From 1449 (when production records start) to the present, ca. 300 000 t of mercury has been mined.

In 1988 Almadén produced ca. 1380 t of mercury. The ore-bearing body has an average mercury content of 5 %. Because of the low price of mercury the plant operates for only a few months of the year. The operating company, Minas de Almadén y Arrayanes SA, is state-owned [5, 6].

Italy. A roughly 25-km-wide, 50-km-long belt running from Monte Amiata to the coast in southern Tuscany contains many closed mines as well as some that are still operating. Although these deposits had been mined by the Etruscans, they were not intensively worked by the Romans, to the benefit of the Spanish mines at Almadén. The Siele mine recommenced operation only in 1846, and the Abbazia San Salvatore mine, at present still the largest, in 1898.

Mercury occurs as cinnabar and metacinnabarite in pyrites, marcasite, antimonite, and realgar, mainly in Eocene sediments (shale, sandstone, marl, limestone) under a covering layer of trachyte. The gangue consists largely of clay or dolomite. The ores contain on average 0.2–0.8 % mercury. Mercury extraction is organized by the Monte Amiata works, its latent production capacity being up to 2000 t/a. No mercury has been mined since 1983.

Former Yugoslavia. The third largest mercury deposits in Europe are situated in Idrija in Slovenia, about 40 km west of Ljubljana. These deposits have been worked since 1497. The mines were under Austrian ownership from 1580 to 1918, then under Italian ownership, and finally reverted to Yugoslavia after World War II.

The tectonics of this region are complicated. Shell marl and shale are impregnated with cinnabar and native mercury, and typically contain admixtures of pyrites, gypsum, and bitumen. The ore contains ca. 0.5 % mercury. Idrija has a capacity of about 600 t/a. About 60 t mercury was mined in 1986. Additional deposits in Yugoslavia are located at Maškara in Croatia, Berg Avala to the south of Beograd in Serbia, Neumarkt in the Karavanen, and Montenegro.

Algeria. Algeria has become the second largest mercury producer in the western hemisphere after Spain, and in 1986 ca. 690 t of mercury was produced.

Germany. In 1936 a modern mercury works was built at Landsberg near Obermoschel in the northern Pfalz (Palatinate), which had to be closed in 1942 because working the very low-grade ore, containing only 0.1% Hg, was uneconomical.

Austria. Fahl ore containing 1.8% mercury is mined in small amounts at Schwaz in the Tyrol. Other deposits at Dollach on the Drava are no longer mined.

Finland. Outokumpu obtains about 100 t of mercury per year from the processing of zinc concentrates.

Former Czechoslovakia. Three important deposits exist: at Kotrbachy, mercury is obtained as a by-product of a fahl ore. Cinnabar is found southwest of Gelnica in a workable ore containing 0.25% mercury. Finally, mercury has been obtained in the region between Mernik and Vranov since the end of the 17th century. This production ceased in 1937.

Romania. Romania has mercury ores at Zlatna and Baboia in Transylvania.

Turkey. In Turkey about 220 t of mercury is obtained annually from mining operations. At present, because of its low price, mercury is extracted from only two mines, which belong to the state-owned Etibank. The deposits are at Izmir-Ödemiş-Haliköy (1×10^6 t of ore containing 0.25% mercury), Konya-Ladik, and Konya-Sizma (1.15×10^6 t of ore containing 0.23% mercury). These deposits alone account for ca. 40% of the Turkish reserves of mercury [7].

Former Soviet Union. The most important deposits in the former Soviet Union are at Nikotovka in the Ukraine. Per year about 400 t of mercury is produced there from an antimonite ore containing 0.4% mercury. Cinnabar deposits have recently been discovered in the Crimea, although no further details are available. Additional ore deposits are mined in the

Northern Caucasus, Urals, Altai Mountains, and in Turkestan and Dagestan.

China. China has important deposits in the provinces of Yunnan, Hunan, and Kweichow. The mines at Wanshantschang and Patschai are well known. Mined production was ca. 760 t of mercury in 1987.

Japan. In Japan, mercury is extracted on the island of Hokkaido.

Canada. Mercury ore deposits are situated in the west of Canada in British Columbia at Pinchi Lake and in the vicinity of Vancouver (Kamloops, Bridge River).

United States. The number of mines in the United States has decreased considerably in the last 20 years. Whereas 149 mines were operating in 1965, only 3 mines were still operating by 1981. The principal mining regions are California and Nevada. Placer, Inc., a subsidiary of the Canadian company Placer Development, accounts for ca. 99% of production. The average mercury content in the ore is 0.3–0.5%. Mining production in 1986 was ca. 400 t and falling.

Mexico. The 200 known mercury ore deposits are distributed over 20 states. The most important mines are in the provinces of Zacatecas, Guerro, Durango, Chihuahua, Guanajuato, San Luis Potosi Aguascalientes, and Quere-taro; total mercury production is some 500 t/a.

South America. South America is of only minor importance as a mercury producer. Chile occupies first place among the mercury-producing countries. The Santa Barbara mine at Huancavelica in Peru is now exhausted, although it supplied substantial amounts of mercury in the 17th and 18th centuries: some 50 000 t was used for precious-metal extraction. Small amounts of mercury are mined in Venezuela and Bolivia.

A U.S. estimate made in 1983 gave the following amounts of mercury extracted by mining operations [8]:

Spain	50 000 t
China	17 200 t
Soviet Union	17 200 t
Yugoslavia	17 200 t

Italy	12 100 t
United States	12 100 t
Other countries	29 000 t
World total	154 800 t

Mining activities and exploitation of deposits are, as with most base metals, greatly dependent on current world market prices. Too low returns have led in recent years to a number of mines being closed, which has resulted in a concentration of plants (less plants with increased production).

17.3.2 Secondary Sources

Like primary ores, industrial waste containing mercury also contributes to its production. The majority of plants used in chlor-alkali electrolysis employ liquid mercury cathodes, resulting in residues containing 10% mercury or more. In addition to this major secondary source, mercury batteries, mercury fluorescent tubes, electrical switches, thermometer breakage, and obsolete rectifiers should be regarded as mercury sources.

Although the overall production of mercury has decreased over the last 20 years, sufficient potential uses and thus secondary sources remain for the foreseeable future, thanks to the unique properties of this metal.

17.4 Production

17.4.1 Extraction from Primary Sources

17.4.1.1 Beneficiation

Preliminary concentration is desirable, especially for working low-grade ores. This is often performed in the mine by classification. Because of the brittleness of cinnabar, pieces of ore break easily at the mercury sulfide veins. Crystalline mercury sulfide in brittle ore can be concentrated by using settling tables.

Another method of concentration is the use of a flotation stage to increase the mercury content. Separation of the antimony and arsenic fractions is particularly important, and

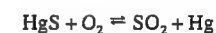
the ores are comminuted to grain sizes of ≤ 0.075 mm (200 mesh) in the case of antimony and ≤ 0.5 mm (25 mesh) in the case of arsenic. After comminution, lead(II) nitrate $[\text{Pb}(\text{NO}_3)_2]$, butyl xanthate, and pine oil are added to the first flotation stage. Flotation is performed at pH 7.1. After purification, mercury is selectively floated, and a concentrate of ca. 50% antimony is obtained. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is added as reactant. The end concentrate has a mercury content of ca. 70% [9]. Another way of concentrating mercury by flotation is to add potassium oleate as collector [10].

Only a coarse preliminary grinding to ca. 50-mm grain size is necessary for high-concentration mercury sulfide ores. During subsequent thermal treatment, the ore particles burst because of the high vapor pressure, resulting in further comminution.

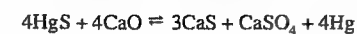
17.4.1.2 Processing to Metallic Mercury [11, 12]

The most important starting material for mercury extraction is mercury sulfide (cinnabar, cinnabarite); it is nonpoisonous and can be stored and transported without any problem.

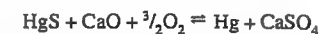
The coarsely ground ore is processed in directly or indirectly heated furnaces, retorts, or muffles. Reaction with oxygen begins at 300 °C, according to



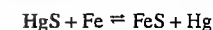
Quicklime can be added as flux to bind the sulfur in solid form. The overall reaction in the absence of oxygen is as follows:



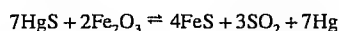
In the presence of oxygen, the reaction is



Addition of metallic iron in the form of iron filings enables the following reaction to occur:



Instead of metallic iron, iron oxides can also be used:



For this reason, sulfur-resistant steel should be used as construction material. Processing is normally performed with the addition of air, and the sulfur dioxide formed can be converted in a downstream wet scrubber.

17.4.1.3 Furnace Systems

Mercury sulfide-containing ores are processed pyrometallurgically. Distinction is made between *directly* and *indirectly* heated furnaces. This is important because the formation of *stupp* cannot be avoided in pyrometallurgical processing (the word *stupp* is an Austrian expression that simply means powder; in the case of mercury, a mercury-containing powder). The greater the formation of dust in the furnace, the greater is the occurrence of *stupp*. Because of the presence of combustion air in the furnace, directly heated furnaces generally create more dust than indirectly heated ones. Mercury in vapor form condenses to some extent on the small dust particles which act as condensation nuclei.

Another difference between directly and indirectly heated furnaces is that mercury vapor in indirectly heated systems is more highly concentrated because it is not diluted by combustion gases.

Directly Heated Furnaces. Cylindrical Bustamente furnaces, multiple-hearth furnaces, and rotary kilns are used.

The *Bustamente furnace* is still used in Spain (Almadén) [5]. The cylindrical vessel is heated outside the shaft, only the combustion gases come into contact with the ore. A historical feature is that mercury vapors are condensed in air-cooled terracotta pipes.

The *multiple-hearth furnace* is advantageous for working up rich concentrates, mercury waste of a similar type, or *stupp*. This kind of furnace has been used for many decades in various mercury mines in North America, and in Almadén most of the ore extracted since 1961 has been processed in multiple-hearth furnaces. The hearths and outer walls of the furnaces are built of shaped fire-

clay bricks. The furnaces are lined with sheet steel. Cast steels with additions of titanium, chromium, and nickel have proved suitable for internal structural elements (stirrer shaft, raking arm). A modern furnace is up to 10 m high, has a diameter of ca. 5 m, and contains up to 16 hearths that are heated with wood, gas, or oil (mainly the upper and lower hearths). An attempt is made to keep the flow velocities for the reaction gas low (maximally 3 m/s) by skillful feeding of the material (if possible by special sliding surfaces at the throats in the case of small hearth interspacings) and by separately installed gas passageways. The amount of flue dust is thereby lowered (0.2–3% of the feedstock), and the formation of *stupp* is minimized. Addition of combustion air through the insulated hollow shaft and raking arm and, if necessary, preheating of the fuel oil both reduce fuel consumption. By accurate metering of the inlet air, a lower amount of gas can be passed through the furnace, and the capacity of the subsequent condensation unit can be reduced. Table 17.4 shows some operational examples of multiple-hearth furnaces.

With regard to environmental protection, multiple-hearth furnaces are relatively difficult to make gastight and, in some cases, have had to be shut down.

Rotary kilns have been used since 1913 to extract mercury. Rotary kilns and rotary drum furnaces provide a high mercury yield with a good throughput rate of the ore because the reaction temperature can be controlled accurately; the ore does not have to be specially preheated; and material throughput can be regulated.

Table 17.4: Operational data for multiple-hearth furnaces for mercury extraction.

	New Almadén	Pershing	Quicksilver Mines
Furnace diameter, m	4.9	4.9	5.5
Number of hearths	6	8	6
Worked material	ore	ore	ore
Throughput, t/d	38	77	50
Fuel consumption per tonne of material	47 L oil	21 L oil	0.15 m ³ wood

The ore is ground to about 65-mm particle size before it is charged. Lime, charcoal, or low-temperature coke may be added as fluxes, and the furnaces are heated directly by oil or gas. The furnaces are operated at 320–400 °C at the charging head and 700–800 °C at the discharge end. For normal furnace sizes and ores, heat consumption is $(1 \text{ to } 1.25) \times 10^6$ kJ per tonne of throughput. Without the addition of coal as flux, this corresponds to up to 30 L of oil or 250 m³ (STP) of fuel gas per tonne of ore throughput. A disadvantage of rotary kilns is the dust formed by the intense material movement, which leads to increased *stupp* formation in subsequent condensation and can cause stoppage in the waste-gas line. Flue dust amounting to 0.75–6% of the ore feedstock by weight is observed. In many cases, dust formation can be reduced by fluxes having a sintering effect. Some operating examples of older rotary kilns are listed in Table 17.5.

Indirectly Heated Furnaces. The basic advantage of indirect heating is the lower gas velocity in the reactor and the higher mercury concentration of the process gas. The furnaces are heated by gas, coal, or by electricity and consist in some cases of clay muffles, vessels lined with fireclay or ceramics, or iron vessels lined with silicon carbide.

F. Krupp-Grusonwerk AG has arranged several tubular individual muffles in a rotary kiln around a thermally insulated, centrally

aligned shaft. A rotary kiln constructed from two concentric tubes was developed several years later. The ore passes continuously through the inner tube; the outer tube is heated. A highly thermally conducting, gastight silicon carbide is used as cladding. Several proposals for processing mercury-containing material in indirectly heated furnaces have been made, and patents have been issued [13–15].

The subsequent condensation of mercury from the furnace off-gas is treated later.

17.4.2 Extraction from Secondary Sources

Because of the relatively high toxicity of metallic mercury and some of its compounds, spent products must be reprocessed to a large extent. Storage of slurry-like residues is complicated and expensive, and is governed by the limited storage capacity of the closed mines. Active carbon slurries from the effluent concentration resulting from chlor-alkali electrolysis constitute the major proportion of mercury residues that must be reprocessed.

In addition to these residues, the processing of fluorescent bulbs, which contain about 15–50 mg of metallic mercury per lamp, is becoming increasingly important. Several plants dealing specifically with the disposal of these lamps already exist in Germany [16].

Table 17.5: Operational data for rotary kilns for mercury extraction.

	Gelnica	Abbadia San Salvatore	New Indria	Nevada, Quick-silver Mines	Pershing, Quick-silver Mines	Mercury Mining Company
Furnace length, m	14	16	17	12.2	18.3	21
Internal diameter, m	1.5	1.25	1.22	0.92	1.22	1.22
Thickness for lining, mm	250	200	150			
Gradient, %	4	5	4			
Time for one revolution, s	72		42	45	50	
Moisture content of ore, %	5–10					
Hg content of ore, %	0.2	0.6–0.8				
Grain size of ore, mm	50	5		64	40	50
Ore throughput, t/d	40	100	125	40	45	45
Fuel consumption per tonne of ore	100 m ³ (STP) gas + 0.3 m ³ wood	100 kg wood	19 L oil	26.5 L oil	30 L oil	29 L oil

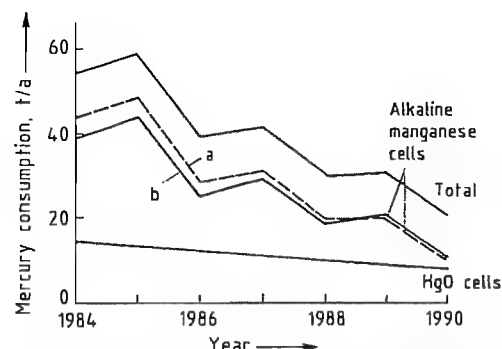


Figure 17.1: Reduction of mercury in primary batteries in Germany [17]: a) Mercury in sold primary batteries; b) Mercury in domestic refuse.

The mercury content of normal zinc-manganese dioxide batteries has been reduced considerably over the last few years (addition of mercury inhibits the formation of gas by zinc). In Germany, the mercury content of batteries will be reduced to 0.15% by 1990 (Figure 17.1), starting from a level of 1% [17].

In addition to zinc-manganese dioxide batteries, zinc-mercury(II) oxide batteries are also widely used as round cells. These contain ca. 30% mercury, which must be recovered. Mercury in concentrations of ca. 1% is also found in zinc-silver(II) oxide and zinc-oxygen batteries. A particular problem in reprocessing batteries is grading and sorting the various types, which are inadequately identified and, in some cases, have the same external dimensions for different electrochemical systems. Treatment processes have been developed in Japan [18], Germany [19, 20], and other countries [21], which can remove mercury by treatment in rotary kilns or in a distillation chamber. The individual types of batteries do not have to be sorted beforehand, and a mixture of batteries can be processed.

Because batteries also include a large number of plastics (e.g., as sealants), waste gases must be treated and burned if necessary.

Because a proportion of spent batteries end up in domestic refuse, high mercury concentrations can be found in waste gas from domestic refuse combustion. Mercury-containing older printing inks are another source. Because mercury can be precipitated

from waste gas most efficiently by adsorption on activated carbon or similar substances, mercury-containing charcoal from waste gas purification will also require reprocessing in the future.

The mercury-selenium residue formed in the primary smelting of mercury-containing sulfidic ores requires special reprocessing. This substance, which occurs as a slurry, has been reprocessed in a multiple-hearth furnace in which the mercury fraction is evaporated [22]. Another company converts the residue to metallic mercury in a rotary kiln by adding lime fluxes, with a relatively inert residue remaining behind [23]. A hydrometallurgical reprocessing treatment has been investigated on a pilot scale in a research project [24]. Mercury is extracted in the form of mercury(II) oxide and sulfide, and can be added to the conventional extraction processes. The method does not appear to be economically practical at present because of the relatively expensive reactants involved.

Additional secondary sources, such as thermometer breakage, electric switches, and amalgams, can generally be worked up by conventional distillation methods [25, 26]. A comprehensive monograph on the topic of evaporation and thermal dissociation of mercury sulfide is available [27]. Electrolysis has been proposed for the removal of mercury from gold-containing solutions: 90–95% mercury and < 10% gold are deposited at 1.0–1.5 V [28].

17.4.3 Condensation of Mercury from Furnace Off-Gas

The vapor pressure p (mbar of mercury) can be calculated according to a relationship given by BARIN and KNACKE [29]:

$$\log p = -\frac{3305}{T} - 0.795 \log T + 10.47893$$

where T is measured in kelvin.

The degree of saturation s (kg of mercury per cubic meter) of the gas at t (°C) or T (K) and $p = 101.3$ kPa can be determined from the

pressure and density of mercury vapor (3.9091 kg/m³ at 357 °C) ($\alpha = 1/273$):

$$s = 3.9091 \frac{1 + 357\alpha}{1 + \alpha t} \frac{p}{101.3} = 3.9091 \frac{630}{T} \frac{p}{101.3}$$

The degree of saturation s of mercury vapor calculated according to this formula for different temperatures is summarized in Table 17.6. Figure 17.2 shows p and s plotted as a function of $1/T$ on a semilogarithmic scale.

Mercury losses during condensation can be calculated as follows: 1 m³ of saturated vapor at 140 °C (413 K) enters the condensation unit laden with 14.464 g of mercury. There it is cooled to 20 °C (293 K) ($s = 0.0141$ g/m³), and a volume contraction to $293/413 = 0.71$ m³ occurs. The saturated vapor leaving the unit therefore contains $0.71 \times 0.0141 = 0.01$ g of mercury. The loss of uncondensed mercury removed with the waste gas is thus 0.07% of the initial amount. With a condensation end temperature of 40 °C and otherwise identical conditions, the loss increases to 0.35% Hg.

Table 17.6: Saturation content of mercury vapor at various temperatures.

p , kPa	T , K	Saturation content, s	
		g/m ³	g/m ³ (STP)
7.03×10^{-5}	283	0.00604	0.00626
1.71×10^{-4}	293	0.01406	0.01508
3.919×10^{-4}	303	0.03144	0.03489
8.514×10^{-4}	313	0.06612	0.07588
1.761×10^{-3}	323	0.1325	0.1568
3.486×10^{-3}	333	0.2545	0.3104
6.625×10^{-3}	343	0.4695	0.5893
0.012138	353	0.8359	1.081
0.02150	363	1.440	1.915
0.03690	373	2.404	3.284
0.06154	383	3.906	5.478
0.100	393	6.187	8.906
0.1585	403	9.558	14.110
0.2457	413	14.464	21.385
0.3727	423	21.417	33.175
2.2894	473	117.65	203.65
3.8743	523	458.97	879.25
32.808	573	1391.5	2921.0
101.3	630	3909.1	9021.1

In practical operation the mercury content in the hot reaction waste gases is always far below the saturation limit because the theoretical vapor-liquid equilibrium is not reached. Directly heated mechanical roasting furnaces

require a heat input of ca. 1.2×10^6 kJ per tonne of ore. The following amounts of waste gas [in m³ (STP)] are produced per 1000 kJ for the different fuels with 20% excess of air:

Wood	0.387
Generator gas	0.42
Oil	0.32

Per tonne of ore, this corresponds to about 470 m³ (STP) with wood or generator gas firing and 375 m³ (STP) with oil firing. With 5% water content in the ore, 70 m³ (STP) of steam is produced in addition. If an ore containing 0.3% Hg is worked up, the mercury content with wood or gas firing is 5.56 g/m³ (STP), and with oil firing 6.75 g/m³ (STP), at 140 °C.

With a condensation end temperature of 20 °C at which the gas still contains 0.0141 g of mercury per cubic meter corresponding to the saturation limit a loss of 0.21–0.25% mercury occurs, and at a condensation end temperature of 40 °C, a loss of 1.1–1.3% mercury from the waste gas occurs.

In general, the mercury residual content in waste gas, compared to the amount at 20 °C, increases with a temperature increase of

10 °C by a factor of 2.2

20 °C by a factor of 4.7

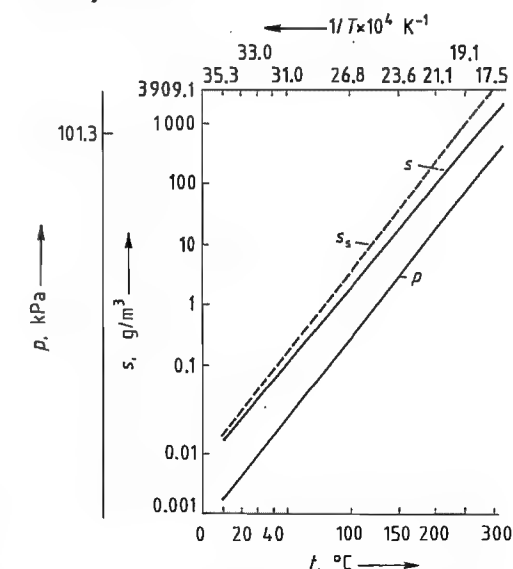


Figure 17.2: Vapor pressure p and saturation content s (g/m³) as a function of temperature; s_s saturation content under standard conditions [g/m³ (STP)].

30 °C by a factor of 9.4
40 °C by a factor of 18.1
50 °C by a factor of 33.4

Thus efficient cooling of the waste gas is necessary. In a plant that processes an ore with 5% moisture content, as much as 50% of the cooler capacity is used for condensation of evaporated moisture alone, without the steam originating from fuel combustion being taken into account.

Several practical requirements must be met for satisfactory operation: (1) The ore should be as dry as possible. (2) The amount of waste gas produced by the fuel should be low. (3) When the gas enters the condenser, its temperature should be only 10–20 °C above the mercury dew point. (4) The outlet temperature should be as low as possible. (5) Before entering the stack, the reaction gas should pass through an afterpurification section, if possible. Stupp formation can be kept low by (1) indirect heating, (2) separate processing of fine-grain classes of ore, (3) predrying of ore that is too wet, or (4) wetting of ore that is too dry. The flue dust should be separated as completely as possible from the still hot reaction gas before it enters the mercury condensation unit.

A conveniently arranged condensation system for a *directly heated* mercury smelting plant operating with mechanical roasting furnaces consists of the following parts:

- Dust separator in the form of a cyclone, an electrostatic precipitator, or a combination of both
- Fan (e.g., of Monel Metal)
- Cooling unit for mercury condensation
- Afterpurification chamber for separating mercury residues
- Injection chamber for separating traces of mercury
- Fan (e.g., of Monel Metal)

The cooling unit is itself in many cases also constructed of monel metal, and consists of tubular condensers (CERMAK type) formed from six to ten trains arranged in parallel, each with eight inverted U-tubes of elliptical cross section whose arms terminate in acutely taper-

ing, water-filled deflection boxes. The tubes are sprinkled with water. The mutually corresponding tubes of all the individual trains in each case end in a common box, and in this way the stupp can be classified. Gate valves in each train enable the draft to be regulated or even permit the train to be separately disengaged.

The ratio of tube cross section to fan output must be matched so that the gas flow velocity is maximally 0.75 m/s in narrow parts of the tubular condenser. The overall unit must be designed so that half of the tube trains can be decommissioned for cleaning and repair, whereas the remaining tube trains ensure satisfactory cooling of the reaction gas while maintaining draft conditions in the furnace.

Gases from *indirectly heated furnaces* that contain only a small amount of flue dust can be condensed by spraying water directly into the mercury-containing waste-gas stream. To ensure sufficient mercury condensation, the gas must pass through a succession of water curtains. Fewer parallel tubes of larger diameter are used in the cooling unit for directly heated furnaces. The last stage operates with fresh water; for the other cooling stages, water is circulated and recycled through suitably dimensioned settling tanks.

All setting tanks within the condensation unit have sloping floors and connecting pipes through which mercury metal flows to the lowest part of the system. The tanks stand on feet on a smooth cement floor, which slopes so that any leakage can be detected and escaping mercury collected. The material for these tanks is wood or cast iron; stupp-collecting tanks are also constructed of concrete. When the plant is operating continuously, all places prone to thick deposits must be mechanically cleaned once a week; the remaining areas can be cleaned at longer intervals.

17.4.4 Treatment of the Stupp

The amount of mercury contained in the stupp may represent a substantial proportion of production. In Idrija, when processing high-bituminous ore, for example, 78–91% of the

mercury is extracted from the stupp and only 9–22% is extracted directly. To extract mercury from the stupp, individual mercury droplets must be coagulated, which can generally be achieved by kneading and pressing the mass. Stirring the stupp with sievelike perforated rakes in iron vessels also gives good results. Addition of quicklime to the stupp neutralizes any acids contained in the condensate, saponifies any fats present, absorbs a large proportion of the water, and chemically reduces mercury sulfate.

Mercury and dust can also be mechanically separated by simple wash treatment with water. A tenfold mercury enrichment from the stupp by *flotation* was described in 1929 [30]. This very effective method of separating mercury enables the waste material to be dumped directly onto the waste tip in certain cases. Generally, however, extraction of mercury from the stupp is not so effective, with the result that the low-mercury fraction must be returned to the smelting process. For regularly occurring large amounts of stupp, a special furnace unit is worthwhile (retorts or multiple-hearth furnace).

17.5 Environmental Protection

17.5.1 Natural Distribution of Mercury

Because of its high vapor pressure, metallic mercury disperses relatively quickly into the atmosphere and, with suitable air movement, is taken up by plants and animals. The average concentration in the earth's crust is 0.08 ppm and in seawater 3×10^{-5} ppm. Mercury is thus one of earth's relatively rare elements. The natural mercury content of the atmosphere is 0.005–0.06 ng/m³ [31]; in plants, 0.001–0.3 µg/g (generally < 0.01 µg/g); and in meat, 0.001–0.05 µg/g [32]. A comprehensive list of mercury in the environment appears in [33].

A quantitative summary of the occurrence, distribution, and utilization of mercury is given in the following material [34]:

Mercury content of the oceans	70 000 000 t
Mercury content of the earth's crust (1-m-thick layer)	100 000 000 t
Natural atmospheric mercury emission (volcanoes, wind erosion, degassing)	25–100 000 t/a
Natural mercury emission in water (weathering in rivers)	5000 t/a
Use of fossil fuels (minerals, deposits)	8–10 000 t/a
Use of mercury and its compounds	6000 t/a

Natural air emissions from mechanical activity, wind erosion, and degassing constitute the largest proportion of emitted mercury. By contrast, the utilization of mercury is relatively small, although this should not minimize or obscure the danger of mercury at high concentration.

17.5.1.1 Mercury in Soil, Plants, and Animals

Relatively large amounts of mercury are circulated due to the constant exchange of mercury among water, soil, and the atmosphere. Some of this migrating mercury is retained in the soil in the form of humus compounds and, in certain cases, is also concentrated [35]. The mercury content of various soils in Austria unless otherwise stated (mg per kilogram of soil) is as follows [36, 37]:

Meadowland in Niederösterreich	0.039
Arable land in Niederösterreich	0.180
Vineyards in the Burgenland	0.080
Reed belt on the Neusiedlersee	0.340
Arable land (3% humus) in Kremsmünster	0.065
Meadowland (4.8% humus) in Kremsmünster	0.070
Woodland (10.2% humus) in Kremsmünster	0.170
Garden soil in England	0.25–15.0
Rice field slurry in Japan	0.40–1.8
Fields for agricultural use in Niedersachsen, Germany	0.055–0.104
Woodland in Niedersachsen, Germany	0.249–1.672
Mean mercury value for Europe (10-cm-thick humus layer)	120 g/ha

Organically bound mercury is also added to the soil with seeds as a seed treatment agent (fungicide). Amounts of mercury used for seed treatment or soil disinfection are as follows:

Grain (wheat) added as seed treatment agent to the soil per 150 kg of seed material/ha	ca. 7 g/ha
Sugar beet (seed material in pill form) added as seed treatment agent to the soil per 200 000 pills/ha	ca. 1 g/ha
Cotton (seed treatment and disinfection)	ca. 20 g/ha

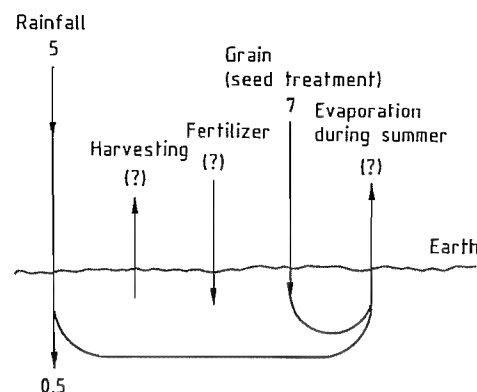


Figure 17.3: Microcirculation of mercury (in gha-1a-1) in the soil [36].

However, neither soils that have received mercury-treated seeds for many years, nor plants grown on such soils, exhibit a high mercury content [35]. As pot tests have shown, the mercury is partly retained in the humus and partly evaporates from the soil [38, 39]. The amount of residue passing into groundwater is insignificant [40] (Figure 17.3).

According to investigations carried out in Norway, the mercury content of soil varies between 0.022 and 0.55 ppm (mean value 0.19), without any "recognizable" effect due to human activity [41]. The mercury content in soil is higher in geothermal or ore-containing regions and can be as high as several parts per million. Thus, mercury is often used as a tracer metal in geological exploration [42].

Mercury content has been investigated in soil and lichen in the mercury mining region around Monte Amiata (Italy). The mercury content in the soil and in the lichen decreases sharply with increasing distance from the mine. Mine waste gases and worked ore are the main sources of emission [43].

Mercury in Fungi and Mushrooms. The fleshy parts of fungi and mushrooms can contain unexpectedly high concentrations of mercury [44, 45]. Because of the affinity of mercury for the sulfur-containing constituents of fungi, the latter can absorb and concentrate mercury from the local soil. Mercury-rich fungi and mushrooms are found everywhere,

regardless of whether the soil has been anthropogenically contaminated [46]. With more serious contamination, especially atmospheric, the mercury content of fungi and mushrooms increases considerably [47].

Mercury in Fish and Seals. The mercury content in fish varies depending on type and habitat [48]. The assumption that fish concentrate mercury to 2000 times its concentration in the ambient medium is neither valid nor statistically relevant and has no significance as a rule of thumb [48]. Mercury uptake in warm, tropical waters is higher than in cold northern waters [49]. Because of the concentration of mercury in sediment, dabbling fish, which collect their food from the bottom of the water, absorb more mercury than nondabbling fish. Predatory fish (e.g., pike) contain higher than normal levels of mercury only if they preferentially feed on dabbling fish.

The controversy surrounding canned tuna in the United States has revealed that tuna preparations in the Smithsonian Institute from ca. 1880 have the same mercury concentration as present-day fish. Under the assumption that the values found in museum preparations constitute a lower limit—some of the mercury might well have evaporated over the course of time—the fact that present-day values are the same as previous values means that no concentration has occurred.

Data from the Danube upstream of large cities and industrial regions, where trout have been found with a mercury content of > 1 mg of mercury per kilogram of fish, point to factors other than industrialization. The high mercury concentration in the liver of seals in the northern section of the east coast of North America (Labrador), where no large cities or industrial regions are to be found, is attributed to underwater volcanic emissions.

17.5.1.2 Mercury in Food

Many investigations were carried out on foods from the 1920s and 1930s onward [50]. In Germany, the Zentrale Erfassungs- und Bewertungsstelle für Umweltchemikalien (central office for collecting and evaluating data on

environmental chemicals; ZEBS) of the Federal Ministry of Health in Berlin in particular, has collected data from 1975, 1979, and 1982. According to these data, if average consumption patterns are assumed, mercury uptake in 1979 was about 0.052 mg per week for the "average" inhabitant of Germany (i.e., only about one-sixth of the upper limit recommended by WHO). The major proportion of mercury is absorbed from animal foods [51]. The legal limits are given in Table 17.7.

The most recent ZEBS investigations [52], covering 1978–1982, are presented in Tables 17.8 and 17.9. The 1982 values essentially confirm the analytical data of 1979. The values for milk, condensed milk, cheese, and eggs; veal, beef, pork, calves liver, calves kidneys, poultry, sausages, and meat products; vegetable oils and fats; rice, rye, and potatoes;

leafy, sprouting, fruit, or root vegetables and canned vegetables; pomaceous, stone, berry, citrus, shell, or canned fruit; fruit and vegetable juices; and beverages such as wine, beer, and chocolate are all < 0.020 mg of mercury per kilogram of fresh substance and, in most cases, < 0.010 mg/kg.

The average amounts of mercury actually absorbed per week are compared in Table 17.9 with the limiting values specified by WHO. Foods contain the major proportion as follows: drinking water (14.8%), wheat (12.9%), milk (10.2%), mineral water (8.1%), canned fish (8.0%), coffee (7.2%), potatoes (6.0%), and fish (5.6%). Another detailed investigation carried out by ZEBS is concerned with the mercury, magnesium, and zinc content of breast milk, blood serum, and the fatty tissue of nursing mothers [53].

Table 17.7: Legal limiting values for total uptake of mercury (1980).

	Fish, mg/kg	Total uptake, mg/week
Switzerland	0.5	
Japan	0.4 (Hg) 0.3 (Hg methyl)	0.17 mg of Hg per 50 kg of body weight
United States	1.0	0.005 mg/kg of body weight (Hg) 0.0033 mg/kg of body weight (Hg methyl)
Sweden	no limit (lakes that contain fish with more than 1 ppm Hg are placed on a blacklist); fish with a high Hg content may be legally rejected.	
Germany	1.0	
WHO recommendation		0.3 (max.)

Table 17.8: Mercury in food.

Food	Content, kg/kg of fresh substance	
	1982	1979
Cow's liver	0.021	0.015
Pig's liver	0.047	0.058
Cow's kidneys	0.077	0.066
Pig's kidneys	0.246	0.260
Freshwater fish	0.271	0.257
Saltwater fish, except Hg-susceptible fish	0.196	0.127
Hg-susceptible fish ^a	1.070	0.859
Fish products	0.208	
Canned fish	0.206	0.188
Wheat	0.026	0.003
Coffee	0.041	

^a Hg-susceptible fish include: mackerel shark, dogfish, blue ling, halibut, black halibut, turbot, and Greenland shark.

Table 17.9: Uptake amounts of mercury in absolute figures and as a proportion of WHO values.

	Hg
WHO value	
mg/week (70 kg)	0.35
mg/week (58 kg)	(0.290)
Men (70 kg)	
mg/week ^a	0.1229
Proportion of WHO figure, %	35.11
Women (58 kg)	
mg/week ^a	0.0933
Proportion of WHO figure, %	32.17

^a The median values of toxic substance levels were taken into account.

17.5.2 Mercury Emissions

17.5.2.1 Gas Purification

In a large number of combustion processes, mercury is transferred to the gaseous phase and must be removed again by subsequent treatment. The largest amounts of secondary mercury occur in the smelting of sulfidic ores. Mercury which is present as mercury sulfide is released during roasting. At present, two methods are primarily used for waste-gas purification.

In the first method, the gas is treated with sulfuric acid (90%) at 200 °C. The mercury(II) sulfate formed is deposited in wash towers. Fine purification is performed by afterpurification with sodium sulfide [54].

In the second method, the cooled and dusted roast gas is treated with a mercury(II) chloride solution, and mercury precipitates as mercury(I) chloride (Hg_2Cl_2). Mercury is removed from the wash liquid by treatment with sodium sulfide. Part of the mercury(I) chloride produced is oxidized to mercury(II) chloride with gaseous chlorine and returned to the process. The final level of mercury in the waste gas is 0.05–0.1 mg/m³ [55, 56].

In a third method, waste gas containing mercury and sulfur dioxide is treated with a wash solution containing Cu^{2+} and Hg^{2+} ions in addition to H_2SO_4 (200–300 g/L) and HCl (5 g/L). Mercury in the vapor is thereby oxidized to Hg^+ , and the Hg^0 values of the waste gas are 0.02–0.05 mg/m³ [57].

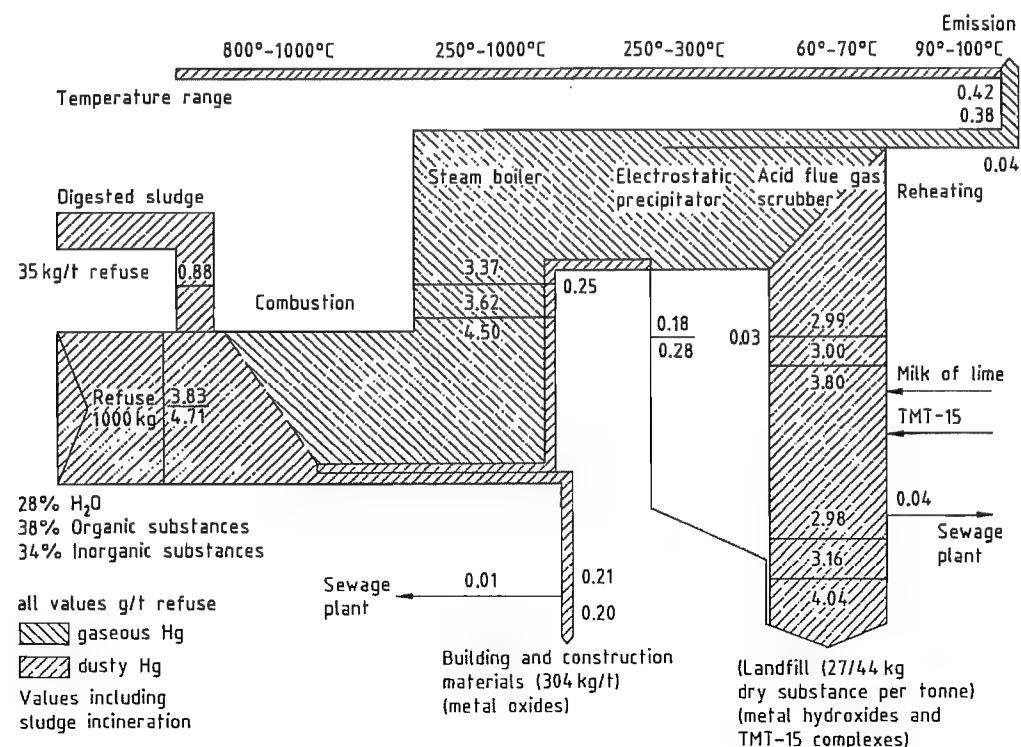


Figure 17.4: Specific mercury load distribution in the Bamberg refuse heating and power station with TMT-15 precipitation, with and without sludge combustion [63].

Another source of mercury emission is refuse combustion. Mercury occurs in the form of thermometer breakage, fluorescent tubes, switches, and batteries in domestic refuse. Investigations have shown that mercury in flue gases is present as mercury(II) chloride [58]. Below ca. 150 °C, the flue ash contained in flue gases adsorbs mercury(II) chloride and reduces it to mercury(I) chloride. Active carbon or active carbon impregnated with iodine compounds can also be used as a mercury adsorbent [59–62]. The mercury content of domestic refuse is 3–5 g/t [63]. The percentage distribution of mercury in a typical refuse combustion plant is shown schematically in Figure 17.4. Most of the mercury passes into the residue to be dumped.

17.5.2.2 Water Purification

The solubility of mercury in water depends strongly on the temperature. It decreases with decreasing temperature and can be reduced further by addition of salts (e.g., sodium chloride).

A whole range of equipment and devices can be used in purification methods to remove mercury from water. Examples are activated carbon filters, ion exchangers, and electrolysis systems. Mercury can also be removed from solution by addition of suitable reagents.

The level of 10–30 mg of mercury per liter in wastewater from chlor-alkali electrolysis can be reduced to 0.1 mg/L by using *activated carbon* and graphite powder. The carbon has a grain size of 5–100 µm [64, 65]. In principle, all types of activated carbon can be used for the fine purification of mercury-containing water. Carbon is dispersed in the water and then filtered.

For *ion exchangers*, a distinction can be made between reusable and disposable ones [65–67]. In some cases, sulfur-containing substances are used as active groups, which remove mercury from the solution in the form of a mercury sulfide compound.

Copper fluidized-bed electrolysis provides another method for mercury separation. The copper powder cathode is held in suspension

by the flowing solution, and mercury is deposited as an amalgam. The copper amalgam is purified by distillation [68].

By adding *small amounts of oil* which are dispersed in the aqueous solution, mercury can be concentrated in the oil phase. The mercury content of the purified aqueous solution is in some cases < 10 µg/L. The oil is separated by centrifugation, and line purification is carried out by using a conventional oil–water emulsion splitting unit. The initial mercury concentration should be between 0.5 and 2.0 mg/L [4]. Tin(II) chloride dissolved in dilute hydrochloric acid has been proposed for treating mercury ion-containing wash water from combustion units. The reducing agent tin(II) chloride is added in above-stoichiometric quantities. Reduced mercury is added together with the wash water to an evaporation device and is expelled by passage of stripping gas at elevated temperature. Condensation is effected by cooling the gas stream. The mercury content is thus reduced from 5 mg/L to < 0.1 mg/L, depending on the concentration of tin(II) chloride [69].

To purify flue gas wash water from *refuse combined heating and power stations*, the additive TMT-15 developed by Degussa is used in some cases on an industrial scale (Figure 17.4). The active substance of the additive consists of trimercapto-*s*-triazine in the form of a sodium salt. Mercury is bound as $\text{C}_6\text{N}_6\text{S}_6\text{Hg}_3$. The compound is stable up to 210 °C and is only sparingly soluble in the elution test (a test to determine the soluble components of a solid material). The mercury content is reduced from ca. 4 mg/L to < 0.05 mg/L [70, 71]. The additional costs involved in TMT-15 precipitation amount to ca. 0.25 DM per tonne of refuse.

Mercury can be removed from *concentrated sodium hydroxide solution* by the use of ultrasound when the solution is filtered. The initial mercury content of ca. 20 mg/kg of aqueous sodium hydroxide is reduced to ca. 0.4 mg/kg after filtration [72].

The fine purification of crude phosphoric acid can be performed at pH 0.5–1.5 by using a diorganodithiophosphorus compound in

conjunction with activated carbon as adsorbent. The final mercury concentration is < 0.02 µg/g of solution [73]. At present, no standard methods exist for removing mercury from sulfuric acid [74].

17.6 Quality Specifications

Fine Purification of Metallic Mercury [75]. Most of the mercury on the market is 4N material (99.99% mercury). Higher purity is seldom required. Impurities in the form of gold (> 10 ppm) are manifested as dark particles after dissolution in nitric acid. Only a few purification methods exist.

- **Dry Oxidation.** In this method, readily oxidizable constituents such as magnesium, zinc, copper, aluminum, calcium, silicon, and sodium can be removed by passing air or oxygen through the liquid metal. The oxides formed have a lower density than mercury and float on its surface. They can be removed by filtration, scooping, or withdrawing the mercury through an opening in the bottom.
- **Wet Oxidation.** In an aqueous medium, mercury is dissolved by adding nitric, hydrochloric, or sulfuric acid with dichromate, permanganate, or peroxide, to oxidize impurities. Good dispersion of the mercury is extremely important in this method. The aqueous solution can be separated from the mercury by decanting, and traces of water can be removed with calcium oxide. A plant for the wet purification of mercury has been described [76].
- **Electrolytic Refining.** Perchloric acid containing mercury oxide serves as the electrolyte.
- **Distillation.** Mercury can be evaporated under atmospheric pressure or in vacuo. Distillation can be carried out in normal steel vessels or in a glass apparatus. Elements with a lower vapor pressure than mercury can be separated in this way. In many cases, mercury must be distilled repeatedly to achieve the desired purity, particularly if it is

to be used to produce cadmium-mercury telluride.

Additional methods, adapted to the relevant processes, are available for purifying and working up larger amounts of mercury [77, 78].

17.7 Chemical Analysis

The oldest and simplest method for determining mercury in minerals is described by Eschka; it involves a gravimetric method in which mercury is precipitated as an amalgam [79]. The ore sample is weighed in a porcelain crucible, intimately mixed with iron filings, and then covered with a layer of zinc oxide, magnesium oxide, or calcium oxide. The crucible is closed with a tightly fitting cover of gold foil having a cup-shaped depression in the middle, which is sprayed from above with cooling water. On careful heating of the sample, mercury is distilled and deposits on the underside of the cover. When a constant weight is reached at the gold foil, all the mercury has been collected. Measurements can be affected by cadmium and arsenic, which also condense on the gold foil. This method of mercury determination requires a high level of experimental skill and care on the part of the analyst, whose technique greatly affects the accuracy and reproducibility of the results. The reliably detectable minimum mercury content is between 10 and 50 ppm. Theoretically, the accuracy could be improved by increasing the amount of sample, although this would give rise to difficulties with regard to the apparatus.

A method for precipitating *monovalent* mercury as an iodate from a neutral or weakly acidic solution (nitric acid) is described in [80]. Mercury can be determined gravimetrically after the mercury(I) iodate precipitate is washed with ethanol and diethyl ether. Parallel gravimetric determination of the excess of potassium iodate precipitation agent is possible with thiosulfate after the mother liquor has been acidified with sulfuric acid and potas-

sium iodide has been added. Both methods give good results.

A quick method for determining mercury(II) is based on the fact that a complex is formed when an excess of potassium iodide is added to a neutral or weakly ammoniacal mercury solution. This complexes with copper diethylenediamine sulfate to form violet crystals of the complex double salt copper diethylenediamine mercury iodide, which is practically insoluble in ethyl alcohol or diethyl ether [81].

In a rapid classical qualitative method for detecting mercury, ca. 1 g of the substance to be tested is digested with acid; the resultant solution is oxidized with a drop of bromine (the solution must not turn yellow) and then boiled with a few milliliters of the reagent (10 g of KI and 100 g of NaOH in 100 mL of H₂O) and filtered. In the filtrate, mercury is determined by the black precipitate formed on dropwise addition of a Sn²⁺ solution [82].

Modern operational monitoring employs physical analytical methods and test tube methods suitable for quick detection. Both *X-ray fluorescence spectroscopy* and *atomic absorption spectroscopy* (AAS) have proved suitable for quantitative and qualitative mercury determination. The detection limit for these methods is so low that the maximum workplace concentration values can be monitored precisely [83].

Portable atomic absorption spectrometers, for example, are available, which indicate the atmospheric mercury concentration as an analog or digital display after a short warm-up time of the spectrometer. The result of the analysis is available immediately and simplifies the monitoring of a production plant. The measurement value can also be recorded continuously at stationary measurement sites with a recorder. The influence of interfering factors in AAS determination is discussed in [84].

Differential pulse anodic stripping voltammetry in conjunction with a gold electrode can be used to detect copper and mercury in natural water and wine [85, 86]. A mercury concentration of 0.02 µg/L can be measured.

Mercury in the air can be detected down to 0.1 ng/m³ with the *Coleman mercury analyzer* system (based on a very selective cold vapor atomic absorption), to an accuracy of 10%. One analysis takes about 3 min [83].

17.8 Storage and Transportation

A classification for the transportation of mercury, mercury oxide, mercury(I) chloride, and mercury(II) chloride is given in [87] (specification sheets 831, 863, 865, 868). DORIAS presents a detailed description of the properties, handling, storage, and transportation of dangerous substances [88], as well as a list of addresses of the relevant authorities (throughout Europe) for information purposes. The provisions differ from country to country and must be ascertained from the relevant authorities.

In general, containers of stainless steel, normal-quality steel, iron, glass, ceramics, and a range of plastics are suitable for storing mercury. When storing liquids that contain extremely low levels of mercury (µg/g-ng/g range) in plastic containers, mercury losses occur with a large number of plastics. When water containing 5 ng/g of mercury was stored in polyethylene bottles, only 5% of the mercury was present after 21 d. Approximately 77% of the mercury had been adsorbed on the side walls, and 18% had evaporated. The Hg²⁺ ions are assumed to be reduced to Hg⁺ ions, which in turn disproportionate to Hg⁰ and Hg²⁺ [89]. Addition of Au³⁺ ions in trace amounts is sometimes recommended [90]. Further investigations on the storage of mercury in dilute solution are discussed in [91–95].

17.9 Uses

Because of its special properties, mercury has had a number of uses for a long time. The conventional application is the thermometer. Mercury is frequently used in pressure gauges and for thermal content measurements.

Table 17.10: Uses of mercury and its compounds [96].

Area of use	Form	Approximate amount, t/a	Emissions	Other sectors, waste elimination	Remarks
Chemicals, reagents	compound	40	laboratories		largely impossible to find suitable replacement; environmental damage can be reduced by other measures
Alkali-manganese batteries	chloride/metal	37		refuse combustion	reduced emission by separate collection possible
Mercury oxide batteries	oxide	20		refuse combustion	alternatives still too expensive; separate collection declining
Pesticides		27	distribution		now only for seed treatment; substitutes are available
Medicinal sector Dental amalgams Disinfection	metal compound	26		refuse combustion	separate collection possible
Fungicides for paints	compound	10	weathering	exploitation; removal of old paint coats	declining; in some cases restrictions on use
Catalysts	compound	8		chemical industry	declining
Thermometers, barometers, manometers	metal	8	instrument and apparatus breakage	refuse combustion	replacement by other methods and processes possible (e.g., electronics)
Electrical engineering components	metal	6		refuse combustion	declining; substitution possible largely through electronic components
interval switches				exploitation of scrap	
Fluorescent tubes	metal	3	lamp breakage	refuse combustion	demand for fluorescent tubes increasing, despite reduction in mercury use per tube; total use increasing
Pigments	sulfide	1		refuse combustion	declining

In mechanical engineering, mercury is used in mercury vapor diffusion pumps for producing a high vacuum.

One important area of use is the lighting industry, where mercury is added to various types of bulbs. Among electrical components, mercury switches, rectifiers, oscillators, and primary batteries can be mentioned, which contain up to 30 % mercury.

Mercury is used as a liquid cathode in the production of chlorine and sodium hydroxide by chlor-alkali electrolysis. Because mercury forms alloys with a large number of metals, mercury alloys have a wide range of applications. Table 17.10 summarizes the areas of use of mercury and its compounds.

17.10 Mercury Alloys

The alloys of mercury (amalgams) occupy a special position among metal alloys because they can be solid, plastic, or liquid at room temperature.

Liquid amalgams are true solutions of the alloying elements in mercury, whereas plastic amalgams are suspensions of solid particles of the alloying partners in mercury or a saturated mercury solution. Solid amalgams are intermediary phases, often mixed with alloying partners or their primary mixed crystals. Solid amalgams may contain liquid-phase inclusions. An amalgam is sometimes difficult to identify experimentally. JANGG has suggested a suitable apparatus for synthesizing and analyzing amalgams [97].

The solubility of many metals in mercury depends strongly on temperature (Figure 17.5). The solubility of some metals in mercury at room temperature is given in Table 17.11. Amalgam formation may be exothermic (e.g., sodium) or endothermic (e.g., gold).

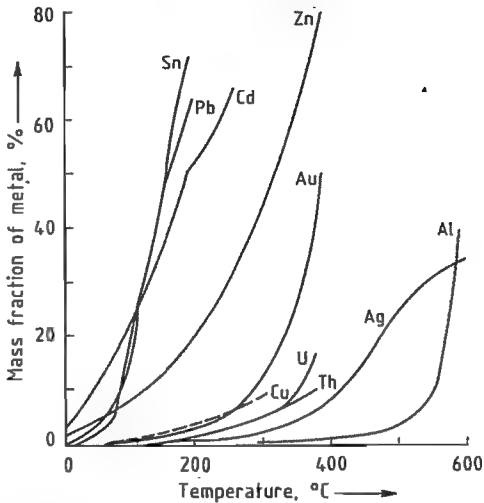


Figure 17.5: Solubility of some metals in mercury as a function of temperature [99].

Table 17.11: Solubility of some metals in mercury at 20 °C [97].

Metal	Solubility, %	Metal	Solubility, %
Tl	42.5	Mg	ca. 0.3
Cd	5.0	Au	0.131
Zn	1.99	Ag	0.035
Pb	147	Cu	ca. 0.002
Sn	ca. 0.9	Al	0.002
Na	0.62	Fe	ca. 10 ⁻⁵
K	ca. 0.4	Si	virtually insoluble

Ammonium amalgam, which has been known for a long time, is an interesting case of the NH₄ group acting as a metal-like alloying constituent. The synthesis of tetramethylammonium amalgam is described in [98].

Technically important amalgams are those of tin-copper precious metals used in conservative dental treatment.

Gold, silver, or tin amalgams are still used for much gold- and silver-plating work, as well as for production of certain types of mirrors. The measurement range of mercury thermometers can be extended to -58 °C by addition of thallium to mercury.

Alkali amalgam is an important intermediate in chlor alkali electrolysis by the amalgam method. Amalgams also play a role in the extraction of cadmium or aluminum [99].

A comprehensive list of thermodynamic data on amalgam formation has been collected by GUMINSKI [100]. After surveying the literature, he is of the opinion that liquid mercury greatly influences intermetallic compound formation. The reactions are comparable to the solid-state formation of ionic and nonionic substances in liquids.

Production of Amalgams. Three methods are used for the industrial production of amalgams:

- **Powder Metallurgy Method.** The powdered alloying components are mixed with mercury. The reaction rate of spontaneously occurring amalgam formation is determined by the degree of dispersion of the powder, the rate at which reactants diffuse into one another, and the wettability of the powder by liquid mercury. If other components besides mercury are added simultaneously, they are preferably pulverized as master alloy in the desired weight ratio. In many cases, the powder reacts with mercury more quickly in the presence of a salt of the element to be amalgamated.
- **Galvanic Method.** Many metals can be deposited from their aqueous solutions or from salt melts on mercury cathodes, with simultaneous formation of an amalgam. Because of the high overvoltage of hydrogen on mercury or amalgam cathodes, even nonprecious metals (Zn, Fe, Mn) can be deposited from acid solutions. Nonaqueous solutions may also be used (with Mg, Ti).
- **Reaction with Sodium Amalgam.** Metal exchange can occur in a fast and stoichiometric reaction through the phase boundary by reaction of sodium amalgam with the salt solution of a precious metal (or, generally, by reacting a nonprecious amalgam with a noble-metal salt solution).

17.11 Compounds

Mercury occupies a special position in group 12 of the periodic table. In contrast to the two other members of this group (zinc and cadmium), it forms compounds in two valence states.

Compounds of *monovalent* mercury contain ions in the unusual form Hg^{2+} . These compounds are not very stable and disproportionate easily to form elemental mercury and the corresponding divalent mercury derivative. Most of the monovalent compounds are sparingly soluble in water. The more soluble salts, e.g., the nitrate, are partially hydrolyzed in aqueous solution: after acidification of these solutions, the poorly soluble compounds can be obtained by precipitation. In addition, compounds of monovalent mercury can be prepared from those of the divalent element by reduction with metallic mercury.

The compounds of *divalent* mercury can be divided into those that are strongly dissociated and those that are weakly dissociated. The former, such as the sulfate and the nitrate, undergo considerable hydrolytic cleavage in water. The weakly dissociated compounds, e.g., the chloride and the cyanide, are less prone to hydrolysis by water. With excess anions they form complexes that are more soluble than the salts themselves.

The starting material for all of these compounds is elemental mercury: the metal is treated initially with a suitable oxidizing agent, e.g., chlorine or nitric acid. The other compounds can be obtained from the resulting oxidation product by further reaction. Multi-step processes are often necessary.

17.11.1 Mercury Chalconides

Chalconides of monovalent mercury are unknown: precipitation from a solution of mercury(I) nitrate with sodium hydroxide does not lead to the expected mercury(I) oxide, but rather to a mixture of finely divided elemental mercury and mercury(II) oxide. The chalconides of divalent mercury exist in na-

ture as minerals: the oxide HgO as montroydite, the sulfide HgS as cinnabar and metacinnabar, the selenide HgSe as tiemannite, and the telluride HgTe as coloradoite. They can also be produced synthetically. Only the oxide and the sulfide are of practical importance.

Mercury(II) oxide, HgO , ρ 11.1 g/cm³, is a red or yellow powder. The color depends on the size of the crystals: the yellow oxide consists of crystals < 2 μm ; the red one of crystals > 8 μm in diameter. Samples with particle sizes between these two values appear yellow-to red-orange. Increasing the temperature leads to an intensification of the color: the yellow oxide becomes yellow-orange; the red one, dark red. The crystal lattice is rhombic and identical for both forms. Under certain preparative conditions a hexagonal form exists. This modification has no practical importance and can be converted to the more stable rhombic form by heating above 200 °C.

Heating above 450 °C causes the oxide to decompose into elemental mercury and oxygen. Mercury(II) oxide is sparingly soluble in water and in ethanol. With dilute mineral acids, solutions of the corresponding salts are formed, a method that can be used to prepare these salts.

Production. Mercury(II) oxide can be prepared via the *anhydrous route* by reaction of the elements at 350–420 °C under oxygen pressure or by thermal decomposition of mercury nitrates at ca. 320 °C. Production via the *wet route* by precipitation is more important: the oxide is precipitated from solutions of mercury(II) salts by addition of caustic alkali [usually mercury(II) chloride solutions with sodium hydroxide]. Whether the yellow or the red form is obtained depends on reaction conditions: slow crystal growth during heating of mercury with oxygen or during thermal decomposition of mercury(I) nitrate leads to relatively large crystals (i.e., the red form). Rapid precipitation from solution gives finer particles (i.e., the yellow form). Nevertheless, depending on the conditions during precipitation such as stirring speed, pH, temperature, and

method of mixing the components, large crystals can be obtained by the wet route and, therefore, the red form is produced [101].

Uses. Red mercury(II) oxide in particular has become increasingly important for the production of galvanic cells with mercury oxide anodes in combination with zinc or cadmium cathodes. These cells are distinguished from other systems in that their voltage remains very constant during discharge; they are used mainly as small button-shaped batteries, e.g., for hearing devices, digital watches, exposure meters, pocket calculators, and security installations. Additional uses of mercury(II) oxide include the following: for the production of mercury(II) salts by treatment with the corresponding acids, and as a reagent in analytical chemistry. Its importance as an additive to antifouling paint for ships and in medicine (e.g., for eye ointment) has decreased.

Mercury(II) sulfide, HgS , is the most important starting material for mercury extraction; it can exist in two forms: α - HgS (*cinnabar*, cinnabarite) has a density of 8.1 g/cm³, and β - HgS (*metacinnabar*) has a density of 7.7 g/cm³. The β -form slowly changes to α - HgS on heating. The latter sublimes at 583 °C. Of the two sulfide minerals, cinnabar is the most important ore for the production of mercury (see Section 17.4.1.2). When pure, the compound is bright red and forms hexagonal crystals. *Metacinnabar* is black and forms cubic crystals (zinc blende lattice). Both have extremely low water solubility; they are also insoluble in mineral acids and in caustic alkali. They dissolve only in aqua regia, to release sulfur, and in alkali sulfide solutions, to form thio complex-salt ions, such as $[\text{HgS}_2]^{2-}$.

Production by either the dry or the wet route is possible. In the former, a mixture of mercury and sulfur is heated. The elements react slowly together even on mixing. Production from aqueous solutions is more important. The sulfide is precipitated from solutions of mercury(II) salts by treatment with hydrogen sulfide, alkali, or ammonium sulfide solutions. Initially, the black sulfide is formed.

It can be converted to the more stable red form by heating in the presence of the mother liquor or with ammonium polysulfide solutions. The reaction of mercury and sulfur by heating with a solution of sodium polysulfide has been described [102].

17.11.2 Mercury Halides

Halides of both mono- and divalent mercury are known. Of these, only the fluorides are ionic compounds: they undergo hydrolysis with water; mercury(I) fluoride simultaneously undergoes disproportionation. The other halides either are already composed of molecules in the crystal lattice or form these by dissolution or evaporation. Accordingly, their melting and boiling points are low. The halides of monovalent mercury are sparingly soluble in water: the solubility of divalent mercury halides decreases with increasing molecular mass. Mercury halides form numerous basic compounds.

Mercury(II) fluoride, HgF_2 , *mp* 645 °C, ρ 9.0 g/cm³, forms colorless octahedral crystals with a cubic ionic lattice (fluorite type). It is unstable in humid air; hydrolysis yields a yellow color. Mercury(II) fluoride is insoluble in organic solvents.

The compound is *produced* from mercury and fluorine at elevated temperature or from mercury(II) oxide and hydrogen fluoride under oxygen pressure at 450 °C [103]. Synthesis from mercury(II) oxide and sulfur tetrafluoride has been suggested [104]. The compound is used in organic synthesis as a fluorinating agent.

Mercury(I) chloride, calomel, Hg_2Cl_2 , ρ 7.15 g/cm³, is rarely found as a mineral in nature. When pure, it exists as a heavy white powder or as colorless crystals with a silvery luster, having a tetragonal molecular lattice. It sublimes at 385 °C; above 400 °C the molecules decompose into a vapor composed of mercury and mercury(II) chloride. The substance is sparingly soluble in water, ethanol, diethyl ether, and acetone. A black color occurs in ammonia solution, whereby a mixture of

finely divided elemental mercury and mercury(II) ammonium chloride is formed by disproportionation—hence, the name *calomel*, from the Greek word meaning beautiful black.

Production. An intimate mixture of mercury and mercury(II) chloride is heated at 525 °C in closed iron or fused silica tubes, attached to cooled receivers in which calomel vapor condenses [105, 106]. Synthesis from the elements is also possible [101]. Very finely divided mercury(I) chloride can be obtained by precipitation from a dilute nitric acid solution of mercury(I) nitrate and sodium chloride [105].

Mercury(I) chloride finds *application* in calomel electrodes, which serve as standard electrodes for the measurement of electrochemical potential; it is also employed as a fungicide and insecticide in agriculture, and as a catalyst in organic synthesis. Mercury(I) chloride is mixed with gold for painting on porcelain.

Mercury(II) chloride, corrosive sublimate, HgCl_2 , *mp* 280 °C, *bp* 303 °C, ρ 5.43 g/cm³, is a white, heavy, crystalline powder with a rhombic crystal lattice. At the melting point the vapor pressure is 560 kPa; the substance can, therefore, sublime under reduced pressure. The sublimate is moderately soluble in cold water. Its solubility increases sharply with increasing temperature: the saturation limit is 6.2% at 20 °C and 36.0% at 100 °C; the compound may therefore be purified by recrystallization from water. The sublimate is readily soluble in organic solvents, in contrast to mercury(I) chloride, so that a clear solution, for example, in ether, is an indication of the absence of calomel. Molecules of mercury(II) chloride exist as such in all solvents; mixing Hg^{2+} ions with Cl^- in aqueous solution leads immediately to undissociated mercury(II) chloride molecules; this process is used analytically to bind chloride ions in determining the COD of effluents. Aqueous solutions of sublimate are weakly acidic, resulting from hydrolysis of a small amount of the chloride. The sublimate is much more soluble in alkali chloride solution than in pure water, because

of the formation of chloro complex ions, e.g., $[\text{HgCl}_4]^{2-}$.

Production. For the formation of mercury(II) chloride from the elements, mercury is oxidized with chlorine in heated retorts; the reaction is carried out with the appearance of flame at > 300 °C. The escaping sublimate vapor is condensed in cooled receivers, where it settles as fine crystals. Formation of mercury(I) chloride is avoided by the use of excess chlorine [101]. Mercury and chlorine also react in the presence of water; in this case, intensive stirring is necessary. The chloride formed precipitates as crystals after the solubility limit has been exceeded. If an alkali chloride solution is used in place of water, solutions of chloro complex salts are formed, which are used mainly for the production of other compounds of divalent mercury [107].

Mercury(II) chloride can also be prepared from other mercury compounds. Mercury(II) sulfate, for example, is heated in the dry state with sodium chloride, and the evolving mercury(II) chloride vapor is condensed to a solid in receivers. A warm sublimate solution is obtained from the reaction of mercury(II) oxide and a stoichiometric amount of hydrochloric acid; the chloride separates as crystals on cooling.

Uses. Mercury(II) chloride is an important intermediate in the production of other mercury compounds, e.g., mercury(I) chloride, mercury(II) oxide, mercury(II) iodide, mercury(II) ammonium chloride, and organic mercury compounds. The compound is used as a catalyst in the synthesis of vinyl chloride, as a depolarizer in dry batteries, and as a reagent in analytical chemistry. It has minor importance as a wood preservative and retains some importance as a fungicide. Other uses (e.g., as a pesticide or in seed treatment) have declined considerably.

Mercury(II) bromide, HgBr_2 , *mp* 236 °C, *bp* 320 °C, ρ 6.05 g/cm³, forms colorless crystals with a rhombic layered lattice. Its water solubility is highly temperature dependent: the concentration limit is 0.6% at 25 °C and 18% at 100 °C. Mercury(II) bromide is readily sol-

uble in diethyl ether and ethanol. The compound is *produced* from mercury and bromine in the presence of water; by dissolution of mercury(II) oxide in hydrobromic acid; or by precipitation from a nitric acid solution of mercury(II) nitrate with addition of sodium bromide [108]. It is used as a reagent for arsenic and antimony, as an intermediate in the production of bromine-containing organomercury compounds (see Section 17.12), and as a catalyst in organic synthesis. The melt is used as a nonaqueous solvent.

Mercury(II) iodide, HgI_2 , exists in a red and a yellow form. Red mercury(II) iodide is soluble in diethyl ether, chloroform, and methanol. The compound is produced by adding an aqueous solution of potassium iodide to an aqueous solution of mercury(II) chloride with stirring; the precipitate is then filtered off, washed, and dried at 70 °C. A yellow product is formed by sublimation; on cooling, it turns red.

Yellow mercury(II) iodide, *mp* 259 °C, *bp* 354 °C, is unstable at room temperature and is converted to the red form at the slightest touch or upon heating. The transition temperature is 127 °C. Yellow mercury(II) iodide is prepared by pouring an alcoholic solution of the red form into cold water, whereby a pale yellow emulsion is formed, from which the mercury(II) iodide crystallizes after a few hours.

Potassium mercury iodide, K_2HgI_4 , readily soluble in water, is prepared by dissolving mercury(II) iodide in a concentrated potassium iodide solution.

17.11.3 Mercury Pseudohalides

The *cyanides* and *thiocyanates* of divalent mercury resemble the halides, in that they also exist in solution as undissociated molecules and form highly soluble complexes with an excess of the anion; moreover, numerous basic compounds are derived from them. Mercury(I) cyanide is unknown; the poorly soluble mercury(I) thiocyanate, which can be obtained by precipitation from mercury(I) nitrate solution, has no practical importance.

Mercury(II) thiocyanate, $\text{Hg}(\text{SCN})_2$, ρ 3.71 g/cm³, is a white powder which is thermally unstable. Decomposition begins at 110 °C and becomes spontaneous at 165 °C, with the compound swelling to many times its normal volume. In air a blue flame appears, and a dark-colored, voluminous residue is left. The thiocyanate is sparingly soluble in cold water. It is produced by precipitation from mercury(II) nitrate solution with a stoichiometric amount of potassium thiocyanate solution and is used as an analytical reagent and as an intensifier in photography.

17.11.4 Acetates, Nitrates, Sulfates

The acetates, nitrates, and sulfates of mercury are composed of ions and undergo hydrolysis with water. The acetate and the sulfate of monovalent mercury are sparingly soluble and the nitrate is quite soluble in dilute acid. Compounds of divalent mercury are readily soluble in dilute acid.

Mercury(II) acetate, $(\text{CH}_3\text{COO})_2\text{Hg}$, ρ 3.27 g/cm³, *mp* 178 °C, exists as a fine white powder or colorless shiny crystal flakes. It is soluble in diethyl ether and ethanol. It is produced by dissolution of mercury(II) oxide in dilute acetic acid and concentration of the resulting solution. Mercury(II) acetate is used for the synthesis of organomercury compounds, as a catalyst in organic polymerization reactions, and as a reagent in analytical chemistry.

Mercury(I) nitrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, ρ 4.68 g/cm³, *mp* 70 °C, which forms colorless crystals (monoclinic ionic lattice), is produced by dissolving mercury in cold dilute nitric acid and crystallizing the compound from the resulting solution.

Uses. Mercury(I) nitrate is the most readily available soluble salt of monovalent mercury and is, therefore, an important intermediate for other mercury(I) derivatives; sparingly soluble compounds can easily be prepared from it by precipitation from aqueous solution. Thermal decomposition leads to red mercury(II) oxide. "Millons reagent", a solution of mercury nitrate and nitrous acid in dilute nitric

acid, is used as an analytical reagent for the indication of tyrosine-containing proteins.

Mercury(II) nitrate, $\text{Hg}(\text{NO}_3)_2$ or $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, forms colorless, hygroscopic crystals. Apart from the anhydrous salt and the monohydrate, several other hydrates and basic compounds are known. Mercury(II) nitrate is produced by dissolving mercury in hot concentrated nitric acid; the resulting solution is concentrated and the nitrate crystallized by cooling. Uses include the production of other divalent mercury derivatives, as a nitrating agent in organic synthesis, and as an analytical reagent.

Mercury(I) sulfate, Hg_2SO_4 , ρ 7.56 g/cm³, is a colorless microcrystalline powder (monoclinic crystal system) that is very sensitive to light. The compound is prepared by precipitation from a solution of mercury(I) nitrate with sulfuric acid or sodium sulfate solution, or by electrochemical oxidation of mercury in dilute sulfuric acid. It is used as a depolarizer in standard cells after Clark and Weston.

Mercury(II) sulfate, HgSO_4 , ρ 6.49 g/cm³, is a white powder (rhombic crystal type). It is prepared by fuming mercury with concentrated sulfuric acid or by dissolving mercury(II) oxide in dilute sulfuric acid and evaporating the resulting solution until the compound crystallizes. Mercury(II) sulfate is used in analytical chemistry to bind chloride ions in the determination of the COD of wastewater [109]; as a catalyst in the production of acetaldehyde from acetylene and of anthraquinonesulfonic acids; and as a depolarizer in galvanic elements.

17.11.5 Mercury-Nitrogen Compounds

Reaction of mercury(II) compounds with ammonia solution leads, depending on reaction conditions, to amine complexes or mercury(II) nitrogen compounds. Of the numerous compounds known, only mercury(II) amidochloride has any practical importance.

Mercury(II) amidochloride, HgNH_2Cl , ρ 5.38 g/cm³, is a fine, white crystalline powder with a rhombic crystal lattice. It is insoluble in water and in ethanol, and soluble in warm acid, ammonium carbonate solution, and sodium thiosulfate solution. On heating it decomposes without melting. The compound can be precipitated from mercury(II) chloride solution with an ammonia solution. Mercury(II) amidochloride is used in the treatment of severe skin disease, as an eye ointment, and as a veterinary preparation; its importance is declining because of the development of mercury-free products.

17.11.6 Analysis, Storage, and Transportation; Protective Measures

Analysis. Determination of the purity of mercury compounds, which consists of the determination of trace amounts of foreign cations and anions, involves specific reactions of these ions [110]. conventional methods for the trace analysis of cations have been supplemented or replaced by methods involving the simultaneous determination of several elements by means of plasma emission spectroscopy [111].

Storage and Transportation. Plastic-lined steel drums are normally employed for packing. Small amounts (e.g., for chemical laboratories) are usually placed in plastic or glass bottles. Many compounds are light-sensitive and must, therefore, be adequately protected from light sources. Proper consideration must be given to the chemical and toxic properties of mercury compounds and the necessary protective measures; this is particularly true in container labeling.

Protective Measures. Most mercury compounds, because of their toxicity, require the same protective measures during production and processing as metallic mercury. Furthermore, environmental protection necessitates appropriate precautions (see Section 17.5).

17.12 Selected Organic Compounds

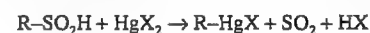
Organic mercury derivatives [112, 113] are among the oldest known organometallic compounds. Organometallic compounds of *divalent mercury* are stable toward air, oxygen, and water. In contrast, organic derivatives of monovalent mercury are unstable and can be prepared only at low temperature. After 1990, use of organic mercury derivatives in Germany will be difficult because mercury will not be allowed in industrial effluent or wastewater.

Organomercury compounds can be divided into two major groups: compounds of the type $\text{R}^1\text{-Hg-R}^2$, where R^1 and R^2 are aliphatic or aromatic groups, and compounds of the type R-Hg-X , where R is aliphatic or aromatic and X is a halogen or an acid group.

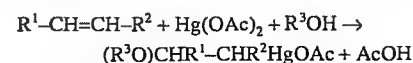
Synthesis of organic mercury compounds can be carried out by reaction of Grignard reagents with mercury halides [114, 115]. To obtain pure products, the mercury salt and the Grignard reagent must contain the same anion

$$\text{RMgX} + \text{HgX}_2 \rightarrow \text{RHgX} + \text{MgX}_2$$

Furthermore, organic mercury compounds can be produced by the reaction of sulfinic acids or their sodium salts with mercury(II) halides [116]:



Hydroxy- or alkoxymercury derivatives can be obtained via the solvomercuration reaction (Hofmann-Sand reaction) by addition of mercury(II) compounds to alkenes in aqueous, alkaline, or alcoholic solutions [114, 117]:



Organic mercury compounds can be converted to other organometallic derivatives by electrolysis or transmetallization [118].

Dialkyl- or Alkoxyalkylmercury Compounds. Dimethylmercury, $\text{CH}_3\text{-Hg-CH}_3$, a colorless, sweet-smelling liquid, is very toxic; it has a density of 3.069 g/cm³, *bp* 96 °C, and is soluble in ethanol and diethyl ether. In acidic aqueous solution, dialkylmercury compounds are hydrolyzed to monoalkylmercury deriva-

tives. Dimethylmercury is formed in organisms by enzymatic methylation of elementary mercury or a mercury compound. In an organism it is easily converted to methylmercury ($\text{CH}_3\text{-Hg}^+$) or methylmercury(II) chloride ($\text{CH}_3\text{-Hg-Cl}$). These species can react with free S-H groups of biologically important molecules, leading to the diseases that have been caused by mercury and its derivatives.

Mixed dialkylmercury compounds (e.g., methylpropylmercury compounds) are less volatile than symmetrical dialkylmercury compounds (e.g., diethylmercury). Dialkylmercury derivatives are generally very reactive and can also undergo transalkylation with simple alkyl halides (e.g., ethyl iodide).

Diarylmercury Derivatives. The best known diarylmercury derivative is diphenylmercury, $(\text{C}_6\text{H}_5)_2\text{Hg}$, which is produced by direct mercurization.

Analysis. Organic mercury compounds may be analyzed in the following ways: they can be determined *qualitatively* (1) by digestion with concentrated sulfuric acid and 30% hydrogen peroxide or (2) by digestion with 10% sulfuric acid and subsequent addition of dithizone (diphenylthiocarbazone) in carbon tetrachloride solution. In the presence of mercury the green solution turns orange. Organic mercury compounds can be determined *quantitatively* by atomic absorption spectroscopy.

17.13 Economic Aspects

A detailed description of the development of production is given in the metal statistics of Metallgesellschaft AG, Frankfurt [119] (Table 17.12). Over the last ten years, production figures have changed only slightly. According to U.S. estimates, current production is ca. 53% of the potential capacity. Because of reduced demand many mines and smelting plants are no longer operating or have greatly cut back production. Intervention by the former Soviet Union has seriously depressed the price of mercury to dumping price levels, although this has been resisted by Spain and Algeria. The change in the price of mercury

since 1979 is shown in Table 17.13 [119]. A survey of previous mercury prices is included in [120].

The main producers of mercury extracted by mining are as follows [121] (figures refer to flasks):

Algeria	23 000
China	20 000
Finland	2 300
Yugoslavia	2 000
Mexico	10 000
Spain	42 000
Former Czechoslovakia	4 400
Turkey	6 000
Former Soviet Union	66 000
United States	14 000 ¹

The Algerian mercury producer, Entreprise nationale des non-ferreux et substances utiles (ENOF), quotes production prices of \$300 per flask. Most of the Chinese production is exported to the United States. China claims to have the largest mercury resources in the world. Guizhou Province contains five mines, accounting for ca. 90% of Chinese production. Italy, once a large mercury producer, now imports mercury from Algeria, the Netherlands, and former Yugoslavia. In Mexico, ca.

¹ The sole producer in the United States discontinued mining operations from the middle of 1987 to February 1988. The production for 1988 is 14 000 flasks.

Table 17.12: Production of mercury in tonnes [119].

	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Europe ^a	1672	1757	1693	1764	1704	1178	1140	135	128	734	475
Spain	1520	1539	1471	1553	1499	967	962	52	36	636	386
Finland	80	130	147	144	135	160	141	74	85	98	89
Yugoslavia	72	88	75	67	70	51	37	9 ^b	7		
Asia ^a (Turkey)	182	226	262	211	97	202	60	25	5		
Africa (Algeria)	586	801	764	756	662	587	639	431	476	459	400
America	1043	965	695	264	724	1065	1195	398	85	82	80
Dominican Republic	2	1									
Mexico	384	394	185	124	345	651	735	340 ^b	21 ^b	12	10
United States	657	570	510 ^b	140 ^b	379 ^b	414 ^b	460 ^b	58 ^b	64 ^b	70	70
Total Western countries	3483	3749	3414	2995	3187	3032	3034	989	694	1275	955
Czechoslovakia	152	158	168	164	168	131	126	75	60 ^b	50	50
USSR ^b	1220	1200	1200	1200	1180	1180	2100	1900	1900	1700	1500
China ^b	800	800	850	900	900	1200	800	780	392	468	408
Total Eastern countries	2172	2158	2218	2264	2248	2511	3026	2755	2352	2218	1958
Total world	5655	5907	5632	5259	5435	5543	6060	3744	3046	3493	2913

^a Excluding Eastern-Bloc countries.

^b Estimates.

350 t of mercury (ca. 10 000 flasks) was extracted from mines in 1986, a large part of the production being exported to Brazil and Argentina. Spanish mercury production is ca. 40 000 fl. The main importers are the United States, Belgium, Luxemburg, and France. The former Soviet Union produces ca. 67 000 fl of mercury; in contrast to the high export level in 1986, almost the entire production is now reserved for domestic use. The capacity of production plants at the Anzob antimony mercury complex in Tajikistan has been doubled. The major proportion of former Yugoslav production of ca. 2000 fl of mercury is exported.

The development of prices and production figures will certainly be influenced substantially by acceptance of the metal mercury, and in large sectors no foreseeable substitute exists. The utilization of mercury in a highly industrialized country such as Germany is shown in Table 17.14 [122]. The purchase of mercury by individual sectors has decreased sharply since 1980. The main user of mercury is the electrical engineering industry, followed by the alkali chloride industry. The use of mercury in paints, pigments, and pesticides has fallen sharply.

Table 17.13: Quoted prices for mercury in London and New York.

Year	European price		U.S. Price	
	£ per flask (34.473 kg)	£/kg	\$ per flask (34.473 kg)	\$/kg
1985	284.02–293.24	8.24–8.51	310.957	9.02
1986	187.49–200.36	5.44–5.81	232.785	6.75
1987	245.64–255.23	7.13–7.40	295.503	8.57
1988	297.17–310.49	8.62–9.01	335.517	9.73
1989	246.43–261.63	7.15–7.59	287.722	8.35
1990	200.91–218.79	5.83–7.22	249.218	7.23
1991	103.33–119.44	3.00–3.46	122.424	3.55
1992	126.85–173.35	3.68–5.03	201.390	5.84
1993	107.02–125.05	3.10–3.63	186.510	5.41
1994	103.23–119.32	2.99–3.46	194.453	5.64

17.14 Toxicology and Occupational Health [123]

Uptake, Mode of Action, Metabolism. The toxicity of mercury depends, among other things, on its state of aggregation and degree of dispersion. Both fine particulate dust containing mercury and mercury vapors are very toxic in comparison to the liquid metal. Various mercury compounds are very potent poisons. Compounds containing divalent mercury are generally more poisonous than monovalent ones. The toxicity of *inorganic* mercury compounds increases with increasing solubility. Still, in most cases, they are less toxic than *organic* mercury compounds.

The toxicity of mercury is based upon its action as a general cell and protoplasmic poison, i.e., bonding to the sulfhydryl groups of proteins; denaturing proteins; damaging membranes; and reducing the RNA content of cells. This leads to blocking of many enzyme systems. The kidneys and nervous system are especially vulnerable. In animal experiments, methyl mercury and mercury(II) chloride cause a dose-dependent suppression of spermatogenesis.

Acute poisoning occurs when mercury ion concentrations reach 0.2 mg per 100 mL of blood. Daily 5-h exposure to inhaled mercury vapor concentrations of 0.1 mg/m³ leads to severe chronic mercury poisoning.

In foods, different mercury concentrations are tolerated: e.g., in the United States, 0.05 ppm; in Germany, 0.1 ppm. Environmental contamination with mercury leads to a critical concentration effect in animals that occupy higher positions in the food chain (large fish and fish-eating sea fowl). In certain fish, concentrations of 10 ppm of mercury and more have been found: fish and clams originating in Japan's Minamata Bay contained up to 9.6 mg of mercury per kilogram. Eggs of wild birds on the Finnish coast contained up to 3.5 mg of mercury per kilogram. Up to 270 mg of mercury per kilogram of organ tissue was found in dead seed-eating birds.

Table 17.14: Breakdown of mercury use (in tonnes) in former West Germany according to sector [122].

	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985
Alkali chloride industry (without changes in stock levels)	128.0	127.0	99.0	103.0	78.0	87.5	87.5	72.0	50.4	46.3	40.7	31.6	41.8
Catalysis	45.0	29.0	9.0	10.0	11.6	4.8	27.5	18.1	14.1	17.9	6.0	4.5	3.9
Paints, dyes	19.5	18.9	5.6	12.4	12.6	12.6	9.1	3.8	3.5	3.8	1.0	0.6	0.3
Pesticides	30.5	33.7	26.6	27.6	28.7	28.5	33.0	31.8	26.7	4.1	19.0	14.0	9.0
Electrical engineering	26.2	42.1	40.6	43.4	40.4	43.5	45.4	51.5	55.0	54.2	53.1	56.2	65.8
Control instruments and apparatus construction	14.8	17.3	8.7	10.3	14.6	13.4	13.3	16.5	15.7	17.1	7.0	6.1	7.2
Chemicals and reagents	25.3	7.0	33.1	45.8	22.0	31.4	43.2	35.5	27.1	53.9	36.2	24.7	
Medicine	24.2	25.2	25.0	26.0	23.9	24.3	24.2	24.2	22.9	23.6	23.5	24.3	24.1
Miscellaneous	32.8	31.1	44.2	46.7	30.0	30.0	30.0	42.1	32.5	35.7	30.1	30.2	30.2
Total	346.3	331.3	291.8	325.2	261.8	276.0	313.2	295.5	247.9	256.6	216.6	192.2	182.3
Total, % (1980 = 100%)	117	112	99	110	89	94	106	100	84	86	73	65	62

Humans are estimated to consume 0.2 mg of mercury weekly in their diet. Mercury uptake with food leads to concentrations in the kidney of < 0.1–3 mg/kg; the corresponding concentrations with intoxication are 10–70 mg/kg.

Amalgam fillings are the most frequent cause of chronic mercury and tin intoxication. The metal is transformed to highly toxic organic compounds by oral microorganisms. During chewing (gum) up to 26 mg/L of mercury and 0.3 mg/L tin may be set free.

After 15 min, the mercury content of the respiratory air increased eightfold.

Toxicity of Metallic Mercury and Inorganic Mercury Compounds. The toxicity of mercury and its compounds depends predominantly on their solubility, which determines absorption and distribution in the organism. Thus metallic mercury and all mercury compounds are toxic, with the exception of red mercury sulfide, which is practically insoluble in the body. Mercury vapor causes acute damage to the lungs and chronic damage to the central nervous system. Mercury salts are caustic to the mucous membranes of the gastrointestinal tract and nephrotoxic when absorbed.

Metallic Mercury. Liquid mercury is not highly toxic; in earlier times, it was used as a treatment for ileus. Thermometers that break in the rectum lead to mercury intoxication only if a wound is created and mercury is pressed into the tissues from which it is slowly absorbed. Granulomas develop when mercury is injected into subcutaneous fat tissue; this can occur in suicide attempts or injuries to the hand caused by broken thermometers. Absorption occurs when the mercury depot is broken up into minuscule droplets, for example, after surgical excision. Occasionally liquid mercury has been injected intravenously, either suicidally [124, 125] or accidentally during intracardiac catheter studies when blood was drawn for blood gas analysis by using mercury-filled syringes. Mercury embolisms resulted, and some of the patients showed symptoms of intoxication. One of

nine patients died after five months as a result of the intoxication. Blindness as a result of occlusion of the central artery also occurred. Antisyphilitic treatment with gray mercury ointment caused numerous intoxications, with all grades of severity being encountered. They resulted from skin absorption and from inhalation of the mercury that vaporized on the skin.

Acute *inhalant poisoning* is very dangerous. In four cases, after several hour's exposure to mercury vapor concentrations of 1–3 mg/m³, acute pneumonitis resulted. Chronic inhalant intoxication can be expected with mercury vapor concentrations of 0.1–1 mg/m³. With < 0.1 mg of mercury per cubic meter, even mild intoxication is improbable. In sensitive persons, an increase in subjective signs (micromercurialism) has been observed at 0.02–0.1 mg/m³ [125].

Mercury Salts. Salts of divalent mercury are more toxic than monovalent ones, regardless of the route of administration. In animal experiments the LD₅₀ after parenteral injection for divalent salts is ca. 5 mg of mercury per kilogram. As a result of their poor absorption, they are much less toxic if administered orally, the LD₅₀ in this case being of the order of 100 mg of mercury per kilogram [126]. Strongly dissociated salts are more caustic and generally more toxic than less dissociated ones. An exception to this is mercury oxycyanide [Hg(CN)₂·HgO], which is highly poisonous even though it hardly dissociates. Cyanide ions may enhance the toxicity.

Acute Poisoning in Humans. Mercury(II) chloride (corrosive sublimate) is one of the strongest corrosive poisons; for adults, oral doses of 0.50–1.0 g (in several cases even 0.2 g) are fatal, even though people have survived after ingesting 5 g. A total of 0.2 g introduced into the vagina can be fatal. Administration of 1.5 g of *mercury oxycyanide* was lethal. The toxicity of *mercury(I) chloride* (calomel) depends on its retention time in the gastrointestinal tract. The lethal dosage for adults is generally 2–3 g; for children, 0.4 g [125]. However, in former times, therapeutically administered doses of 0.1 g of mercury(I) chloride have led to death, especially when the

laxative effect did not occur. Chronic intoxication with mercury salts is unusual; in industrial poisonings, exposition to mercury vapors generally exists concomitantly. Mercury salts act as direct skin irritants. Furthermore, they are sensitizing, especially mercury fulminate.

Toxicity of Organic Mercury Compounds. Most organic mercury compounds are lipid soluble. Some of them vaporize easily and thus also act in the gaseous phase. Organic mercury compounds can cause toxic dermatitis and, as a result of their lipid solubility, can severely damage the central nervous system. Hypersensitivity reactions, as well as kidney damage, also occur.

In the organism, *phenylmercury* and *alkoxyalkylmercury* compounds are metabolized to inorganic mercury compounds and act like mercury salts. The stable alkylmercury compounds are neurotoxic and embryotoxic.

Alkylmercury Compounds. Numerous toxicity studies on animals have been reported. The LD₅₀ in rats and mice of most methyl- and ethylmercury compounds is 10–30 mg of mercury per kilogram. This holds true for parenteral and oral administration [126]. In humans, almost all alkylmercury poisoning has been caused by contaminated food, almost all involved chronic poisoning, the dose ingested is unknown, and estimated values are questionable. Mass poisoning in Iraq was caused by pita bread baked with flour made from seed grain; the grain contained ca. 15 mg of mercury per kilogram of alkylmercury (mainly methylmercury) salt.

The bread weighed 220 g and had a water content of 31 %. Affected adults are estimated to have eaten six to eight loaves per day; the first fatalities occurred six to eight weeks after distribution of the seed grain [126, 127].

Minamata disease developed in fishermen and their family members who ate fish daily or at least several times a week, consuming 250–500 g of fish with each meal. The average methylmercury concentration of the fish eaten is not known (estimates: 5–20 mg of mercury per kilogram of fish). Thus, a daily uptake of 1.5–4 mg of mercury would have resulted, re-

spectively [4]. Affected patients had mercury concentrations of 200–2000 µg/L in their blood and 50–500 mg/kg in their hair [128]; the brain of patients who died contained > 5 mg of mercury per kilogram [126]. Mild symptoms are assumed to occur with concentrations of 100 µg of mercury per liter of blood and 30 mg of mercury per kilogram of hair. Daily ingestion of 5 µg of mercury per kilogram of body weight in the form of methylmercury compounds is considered the minimal toxic dose [128].

Mercury is *mutagenic*, *teratogenic*, and *embryotoxic*, especially in the form of alkylmercury compounds [129, 130]. The fetus is three to four times more sensitive to methylmercury than the pregnant woman [128]. Congenital brain damage occurred in 5–6% of the children from Minamata Bay, where the rate expected was 0.1–0.6%. The mothers belonged to the group of people heavily exposed to methylmercury but did not show any clear symptoms of intoxication [126].

Arylmercury Compounds. In animal experiments, arylmercury compounds are as toxic as alkylmercury compounds when administered parenterally; administered orally, however, they are less toxic. As a result of their instability they act like a combination of organically bound mercury and mercury vapor. In adults, ingestion of 100 mg of mercury in the form of phenylmercury nitrate led to abdominal pain and mild diarrhea; however, 120 mg was also tolerated without symptoms. Even after ingestion of 1.25 g of mercury, clinical chemistry values and kidney biopsy results were normal. Concentrations > 0.6 g/L are locally caustic [126].

Antagonism. Mercury and selenium are antagonists; within certain limits, selenium can reduce the toxicity of inorganic and methylmercury. In animal experiments, selenium predominantly delays the appearance of intoxication symptoms but reduces the lethality only slightly. Whether a high dietary selenium content can protect against methylmercury poisoning is still open to question: the fish that caused Minamata disease

contained, in addition to large amounts of mercury, a high proportion of selenium [128, 131].

Occupational Health. The MAK value for metallic mercury in Germany is presently 0.1 mg/m³ (0.01 ppm); for mercury vapor the MAK value is 0.05 mg/m³ [123]. The TWA of mercury is 0.05 mg/m³. The theoretically possible vapor pressure concentration can, however, far exceed this value. The odor threshold for mercury is 13 mg/m³.

The legal requirements covering industrial safety and hygiene when working with mercury and its compounds depend on the laws of individual countries. The measures adopted by a highly industrialized country such as Germany are described below.

The special safety measures for handling and working with mercury-containing materials are given in the TRgA (Technische Regeln für gefährliche Arbeitsstoffe; technical regulations for dangerous substances). They do not cover mercury(II) sulfide, inorganic compounds containing < 0.1 % mercury, or organic compounds containing < 0.05 % mercury. The working methods and procedures must basically be designed so that employees are not exposed to mercury vapor, mist, or dust. Further details are given in [132].

A series of specification sheets for handling mercury has been published, which describes the technical and personal safety measures to be adopted [133]. Explanatory information and instructions for work and health safety are summarized in a comprehensive poisons list [134].

Persons working with mercury should be monitored regularly. With metallic mercury, inorganic mercury compounds, and organic nonalkyl mercury compounds, mercury values in urine should not exceed 150 µg/L. The blood levels should be < 35 µg/L. With organic alkylmercury compounds, the limiting blood level is 75 µg/L.

17.15 References

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18 Cobalt

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18.1 Introduction [1–3]

Cobalt is a metallic element whose electronic configuration is $3d^7 4s^2$ beyond the argon core, giving it an atomic number of 27. The relative atomic mass of cobalt is 58.9332. Only one of its isotopes, ^{59}Co , is stable and occurs naturally; the other 12 known isotopes are radioactive and have the following mass numbers (half-lives in parentheses): 54 (0.2 s), 55 (18.2 h), 56 (80 d), 57 (270 d), 58 (9 h), 58 (72 d), 60 (10.1 months), 60 (5.3 a), 61 (99 months), 62 (1.6 months), 62 (13.9 months), and 64 (< 28 s).

The γ -rays emitted in the decay of ^{60}Co have energies of 1.17 and 1.33 MeV, and these taken with the 5.3-a half-life of the isotope provide a widely used source of radioactivity for use in food sterilization, radiography, and radiotherapy as an external source. The isotope is also used in chemical and metallurgical analysis and in biological studies as a radioactive tracer. The ^{57}Co isotope decays by electron capture to give ^{57}Fe , the most widely used

isotope in γ -resonance (Mössbauer) spectroscopy [4].

Pure metallic cobalt has few applications, but its use as an alloying element and as a source of chemicals makes it a strategically important metal. End uses of cobalt-containing alloys include superalloys for aircraft engines, magnetic alloys for powerful permanent magnets, hard metal alloys for cutting-tool materials, cemented carbides, wear-resistant alloys, corrosion-resistant alloys, and electrodeposited alloys to provide wear and corrosion-resistant metal coatings. Cobalt chemicals, among their many applications, are used as pigments in the glass, ceramics, and paint industries; as catalysts in the petroleum industry; as paint driers; and as trace metal additives for agricultural and medical use. About 36% of the worldwide annual production of cobalt is converted to chemicals, whereas high-temperature and magnetic alloys account for 41% and 14% of the consumption, respectively. Detail on all aspects of the science and technology of cobalt in general reviews [1–3]

can be supplemented by reference to journals of abstracts published between 1975 and 1985 [5] and restarted in 1984 [6, 7].

18.2 History

Although very little cobalt metal was used until the 20th century, its ores have been used for thousands of years as blue coloring agents for glass and pottery. Blue glazed pottery found in Egyptian tombs and dated at ca. 2600 B.C. has been found to contain cobalt, as have Persian glass beads dating from 2250 B.C. The Portland vase in the British Museum provides evidence that cobalt pigments were used by Greek glassworkers around the beginning of the Christian era. Cobalt-containing materials were also used to impart blue coloration to Chinese pottery during the Tang (600–900 A.D.) and Ming (1350–1650 A.D.) dynasties and to Venetian glass produced in the first part of the 15th century. The brilliant blue pigment used for these purposes can be produced by fusing an ore containing cobalt oxide with potash and silica to produce a vitreous material called smalt, which is powdered to produce the pigment. The secret of making the pigment was apparently lost during the Middle Ages and rediscovered during the 15th century. LEONARDO DA VINCI was one of the first artists to use the rediscovered blue pigment when painting "The Madonna of the Rocks". In the 16th century, P. WEIDENHAMMER produced a blue pigment, which he called zaffre, from the silver-cobalt-bismuth-nickel-arsenate ores found in Saxony. The next development in the use of cobalt-containing materials was the discovery, early in the 18th century, that solutions containing bismuth and cobalt could be used as sympathetic inks. The invisible writing obtained by using the inks became green when heated, with the color change apparently due to the presence of cobalt. It was not until 1735 that G. BRANDT, a Swedish scientist, first isolated cobalt metal as an impure sample by reducing an ore; in 1780 T. O. BERGMAN showed that the metal was in fact an element. The use of cobalt as a metal dates from 1907, when E.

HAYNES patented a series of cobalt-chromium alloys named Stellites that were the forerunners of modern superalloys. In 1930 it was shown that addition of cobalt to certain alloys of iron, nickel, and aluminum enhanced their properties as permanent magnets.

From the 16th to the 19th century, the world's supply of cobalt — mainly as smalt and zaffre — was produced in Norway, Sweden, Hungary, and Saxony. Outside of Europe cobalt-containing ores were worked in Burma from 1651 and in New Caledonia from 1864. Major developments in cobalt recovery in the 20th century have stemmed from the discovery of new ore bodies and improvements in the methods of winning the metal from ores. Cobalt-containing copper ores were discovered in Zaire in 1914, and extraction of cobalt from the ores began in 1924, whereas recovery of cobalt from pyrite roasting residues was started in Germany in 1926. Mining of cobalt-nickel-gold-silver ores began in Morocco in 1932, and production of cobalt from copper-cobalt ores began in Zambia in 1933. The Outokumpu copper-cobalt-zinc deposit was discovered in 1913 and has been exploited on a large scale since 1928. In 1940 the International Nickel Co. (INCO) introduced a method of recovering cobalt from nickel ores, and from 1952 to 1955 the production of cobalt by the Canadian companies, Falconbridge Nickel Mines and the Sherritt Gordon Mining Co., began. Recent developments include the commissioning in 1975 of a cobalt refining plant based on a combination of pressure leaching, solvent extraction, and electrowinning by the Sumitomo Metal Mining Co. in Japan.

Worldwide production of cobalt ores in 1980 was 32 700 t of contained cobalt, of which 14 700 t was from Zaire, about 3000 t each from Australia, New Caledonia, and Zambia, about 2000 t from the former Soviet Union, and about 1600 t from Canada.

The production of cobalt is usually subsidiary to that of other metals, such as copper and nickel, and its output cannot be significantly increased without a corresponding increase in the markets of the primary metals. Another

important factor in the economics of the supply of cobalt is the fact that a large proportion of the world's ore comes from one country, Zaire, and is therefore dependent on the political stability of that country. Cobalt is regarded as a strategic metal and is stockpiled in some countries.

The name cobalt is derived from the Greek word κόβαλος or the German word Kobold for goblin or evil spirit. The term Kobold was applied by miners in the Harz mountains of Germany to an ore that gave no metal when smelted and that also produced highly toxic fumes of arsenic oxide.

18.3 Physical Properties

The physical and mechanical properties [1–3] of cobalt metal are susceptible to variations because of variations in the structures of metal samples arising from a slow cubic to hexagonal phase transformation. The data quoted in this section are for the highest purity metal available; details of the effects of impurities on the properties of cobalt are to be found in a review by W. BETTERIDGE [8].

Cobalt exists in two allotropic modifications, a close-packed hexagonal ϵ -form stable below ca. 400 °C and a face-centered cubic α -form stable at high temperature.

The transformation temperature is 421.5 °C. The free energy change associated with the transformation is low, being ca. 500 J/mol for the $\epsilon \rightarrow \alpha$ change and ca. 360 J/mol for the $\alpha \rightarrow \epsilon$ change; this accounts for the slowness of the transformation. The mechanism of the phase change is martensitic and involves dislocation movements on the octahedral planes of the cubic lattice. Grain size affects the stability of the two allotropes, with finer grain size favoring the cubic high-temperature form. For this reason the fine grain sizes found in cobalt powders, sponge, thin films, and fibers are responsible for the retention of essentially cubic structures down to ambient temperature. The cubic form is also favored by the presence of a few percent of iron in the lattice. Table 18.1 shows the cell

parameters and other properties of the allotropes. The density of the metal decreases with increasing temperature and shows an anomalous fall of ca. 0.15% at the transformation temperature. The liquid density just above the melting point is 7.73 g/cm³, and at 2000 °C it is 7.26 g/cm³.

Table 18.1: Properties of the allotropic forms of cobalt.

Hexagonal ϵ -form	
Cell dimensions (ambient temperature)	$a = 0.25071$ nm
	$c/a = 1.6233$
(417 °C)	$a = 0.2541$ nm
	$c/a = 1.631$
Density (20 °C)	8.832 g/cm ³
Co-Co interatomic distances	0.294–0.251 nm
Stacking fault energy (20 °C)	31×10^{-7} J/cm ²
(370 °C)	20.5×10^{-7} J/cm ²
Cubic α -form	
Cell dimension (ambient temperature)	$a = 0.35441$ nm
(520 °C)	$a = 0.35688$ nm
(1398 °C)	$a = 0.36214$ nm
Density (ambient temperature)	8.80 g/cm ³
(1495 °C)	8.18 g/cm ³
Co-Co interatomic distance	0.251 nm
Stacking fault energy (500 °C)	13.5×10^{-7} J/cm ²
(710 °C)	18.5×10^{-7} J/cm ²

Thermal Properties. The melting point of cobalt is 1495 ± 2 °C, and its boiling point at normal pressure is 2800 ± 50 °C. The vapor pressure of cobalt varies from less than 10^{-5} Pa (at 1250 °C) to greater than 10^5 Pa (at 3200 °C). The heats of fusion and vaporization of cobalt are 17.2 and 425 kJ/mol, respectively. The thermal conductivity (λ) of the metal falls steadily with increasing temperature; there is no marked change in conductivity at the transformation temperature, but the data show a minimum in the region of the Curie temperature at 1121 °C. The values of λ at 0, 100, and 800 °C are 102, 85, and 50 Wm⁻¹, respectively. The heat capacity of cobalt rises steadily with increasing temperature. There is only a slight inflection in the c_p vs. T curve at the transformation temperature, but a large change does occur at the magnetic transformation. The thermal expansion coefficient of hexagonal cobalt depends on the orientation of the crystals being, for example, 14.62×10^{-6} K⁻¹ along the $\langle 0001 \rangle$ and 10.96×10^{-6} K⁻¹ along the $\langle 1120 \rangle$ direction (at 20 °C). The av-

erage value for polycrystalline cobalt is $12.14 \times 10^{-6} \text{ K}^{-1}$. The curve of the coefficient vs. temperature shows a sharp change at the transformation temperature because of the volume expansion of ca. 0.36% associated with the phase change from hexagonal to cubic crystals. Cubic cobalt has a higher mean thermal expansion coefficient with values of (14.2, 15.7, 16.0, and $16.8 \times 10^{-6} \text{ K}^{-1}$ at 200, 400, 600, and 750 °C, respectively.

Mechanical Properties. The mechanical properties of cobalt are critically dependent on the purity of the metal and its thermal history. For well-annealed samples of high-purity cobalt, the *Vickers hardness* at normal temperature has values between 140 and 160 N/mm². The Vickers hardness of annealed cobalt decreases with increasing temperature to values of under 50 N/mm² at 750 °C with no marked change at the phase transformation. Microhardness studies on zone-refined single crystals of the metal show variations with crystal orientation and give values between 81 and 250 N/mm². Electrodeposited cobalt has high hardness (270–310 N/mm²), presumably because of its fine grain size.

Table 18.2: Elastic moduli at 20 °C for cobalt along different crystal directions.

Crystal direction	Young's modulus, 10 ³ MN/m ²	Shear modulus, 10 ³ MN/m ²
1120	174	62.2
1010	175	62.2
1012	169	74.1
0001	213	62.4

Measurements of elastic properties on polycrystalline bars of high-purity sintered metal annealed at 1000 °C give a *Young's modulus* of $211 \times 10^3 \text{ MN/m}$ and a *shear modulus* of $82 \times 10^3 \text{ MN/m}$ at room temperature. The moduli decrease with increasing temperature, with the shear modulus showing an inflection and the Young's modulus a hysteresis at the phase change. For single crystals the moduli do vary with crystal direction, as shown in Table 18.2. Values of *Poisson's ratio* for cobalt are found to be in the range of 0.29–0.32.

Vacuum-melted, hot-worked cobalt annealed at 800–1000 °C has *tensile strengths* of 800–875 MN/m² and an elongation of 15–30%. Air-melted samples are much less ductile. Cobalt has a maximum *ductility* at 500 °C, and this is the best working temperature for the metal, although the vacuum-degassed metal free from lead, sulfur, and zinc, can be hot-rolled in the temperature range of 600–1000 °C. Both elongation and tensile strength values show changes at the phase transformation.

The activation energy for *creep* is higher for hexagonal cobalt than for the cubic form; the values near the phase change temperature are 540 and 190 kJ/mol, respectively. The hexagonal crystals have lower values of friction and wear than the cubic crystals. The *friction coefficient* of cobalt rises steeply at temperatures above 300 °C to values of ca. 1.6 at 400 °C. The low coefficient associated with the hexagonal form is due to easy slip on the basal plane accompanied by the formation of a surface layer with the basal planes oriented parallel to the surface. In actual applications, however, the frictional and wear behavior of the metal will be determined by surface oxide films.

Magnetic Properties. Pure cobalt has the highest known Curie temperature. Hexagonal cobalt is ferromagnetic at all temperatures, but the cubic form becomes paramagnetic at $1121 \pm 3 \text{ °C}$. The magnetic properties of single crystals show marked anisotropy. For hexagonal crystals at ambient temperature, the *c*-axis is the direction of easiest magnetization, but with increasing temperature magnetization becomes easier in a direction perpendicular to the *c*-axis; however, at ca. 250 °C the metal is magnetically isotropic. At even higher temperature, the *c*-axis becomes the most difficult to magnetize. Near the phase change temperature, the direction of easiest magnetization of the cubic form is along the $\langle 111 \rangle$ cube diagonal. Differences between this and other directions diminish with increasing temperatures until, at 1000 °C, the cubic form is magnetically isotropic.

The magnetic properties of polycrystalline samples of cobalt depend on the purity of the metal and its thermal history; this applies particularly to the development of preferred orientation. Magnetic anisotropy can, for example, be developed by slowly cooling the metal over the phase transformation temperature range in a strong magnetic field. Typical values for magnetic property parameters are listed in Table 18.3. The magnetostrictive behavior of cobalt is also strongly anisotropic and reaches a maximum value for hexagonal crystals of $\Delta l/l = -27 \times 10^{-6}$ in a magnetic field of 560 kA/m along the $\langle 1120 \rangle$ direction. The volume magnetostriction shows a maximum contraction of 10^{-6} in a field of 480 kA/m and a magnetostrictive expansion when the fields are above 760 kA/m.

Table 18.3: Magnetic properties of cobalt.

Curie temperature	1121 °C
Maximum permeability	$3.1 \times 10^{-4} \text{ H/m}$
Coercive force	707 A/m
Remanence	0.49 T
Saturation magnetization	1.79 T

Table 18.4: Electrical resistivity and temperature coefficient of resistivity for cobalt.

Temperature, °C	Resistivity, $\times 10^{-8} \Omega \text{ m}$	Temperature coefficient, $\times 10^{-11} \Omega \text{ m/K}$
–100	2.65	—
–50	3.84	—
0	5.25	30
50	6.81	34
100	8.52	39
200	12.80	50
300	18.38	60
400	24.72	71
500	30.65	75
600	39.1	87
800	57.9	105
1000	78.5	100
1200	92.7	41
1400	100.0	34

Electrical Properties. The electrical resistivity and the temperature coefficient of the resistivity of high-purity (99.999%) polycrystalline cobalt are given in Table 18.4. The cubic form has a lower resistivity than the hexagonal modification whenever the forms coexist. The resistivity of single crystals of co-

balt shows a marked dependence on orientation.

Other Properties. The self-diffusion of cobalt in the temperature range between 1057 and 1306 °C follows an Arrhenius-type law, the *diffusion coefficient* being given by the formula $2.2 \times e^{-295/RT}$. The rate of diffusion is very dependent on grain size, being about 10 times faster for powder-metal samples than for bulk samples prepared by melting.

The *optical reflectance* of polished cobalt at ambient temperature and near normal incidence increases with wavelength from 60% (at 1 μm) to 97% (at 12 μm). The reflectance is much less at high angles of incidence. The optical emission spectrum of cobalt is complex and has over 330 lines in the range of 974–201 nm. The most important lines for analytical purposes are listed in Table 18.5. The characteristic $K\alpha_1$, $K\alpha_2$, and $K\beta_1$ X radiation from a cobalt target occur at 0.1789, 0.1793, and 0.1621 nm, respectively; the K absorption edge is at 0.1608 nm.

Table 18.5: Optical emission lines of cobalt used in atomic emission analysis.

Wavelength, nm	Relative intensity	
	Arc source	Spark source
352.9813	1000	30
346.5800	2000	25
345.3505	3000	200
340.5120	2000	150
251.9822	40	200
238.8918	10	35
237.8622	25	50
236.3787	25	50
230.7857	25	50
228.6156	40	300

18.4 Occurrence [1, 2, 9]

Cobalt occurs in nature in a widespread but dispersed form in trace quantities in many rocks, soils, and plants. It is also found in sea water and in manganese-rich marine nodules. The cobalt content of the earth's crust is about 20 mg/kg, whereas its concentration in sea water has been reported as being 0.1–1 part in 10^9 . The concentration of the element in marine nodules is usually 0.1–1%. The largest concentrations of cobalt are found in mafic

and ultramafic igneous rocks; the concentration of the element and the nickel cobalt ratio decreases from ultramafic to acidic rocks, as shown in Table 18.6. The nickel cobalt ratio changes because cobalt enters the lattice of early crystallizing magnesium silicates less readily than nickel. Sedimentary rocks contain varying amounts of cobalt, with average values of 4, 6, and 40 mg/kg being reported for sandstone, carbonate rocks, and clays or shales, respectively. During the formation of metamorphic rocks, very little movement or concentration of cobalt took place; thus, the levels of cobalt found in metamorphic rocks depend essentially on the amount of the element in the original igneous or sedimentary source. Those formed from ultramafic or mafic sources contain an average cobalt content of ca. 100 mg/kg, whereas gneissic granites and metasedimentary rocks contain an average of 16 and 8 mg/kg, respectively.

Table 18.6: Average cobalt content of igneous rocks.

Rock type	Cobalt content, mg/kg	Ni-Co ratio
Ultramafic	270	7
Gabbro	51	2.6
Basalt	41	2.5
Diabase	31	2.3
Intermediate igneous	14	1.9
Felsic	5	1.1

Under oxidizing conditions, cobalt shows a strong tendency to concentrate with manganese oxides. In the weathering process of mafic and ultramafic rocks to form laterites, nickel tended to be leached downward with magnesia and silica, whereas cobalt with manganese oxides was residually enriched near the surface of the deposit. The concentration of cobalt and other metals in marine nodules has been attributed to the strong ion-exchange properties of the submicroscopic particles of colloidal manganese dioxide from which the nodules were formed.

Cobalt is a major constituent of about 70 minerals [10] and is a minor or trace constituent of several hundred more, particularly those containing nickel, iron, and manganese. The minerals that have been mined or concentrated for their cobalt content and those that are rela-

tively high in cobalt are listed in Table 18.7. The sulfide minerals include the copper-containing carrollite, which is one of the main sources of cobalt in Zaire, linnæite found in Zaire, Zambia, and the United States, and cattierite, which is also present in ores from Zaire. The arsenide ores include smaltite, which is found in the silver-copper ores from Cobalt, Ontario and in Morocco, and skutterudite, the main cobalt mineral in Canadian and Moroccan deposits. The sulfoarsenide, cobaltite, is found in ore bodies in Zaire, Canada, and the United States. The oxide mineral heterogenite is a hydrated metal oxide containing varying amounts of cobalt and copper and is one of the main cobalt-bearing components of the Zaire deposits. The hydrated manganese-cobalt mineral, asbolite, is the source of most of the cobalt in ores from New Caledonia.

Table 18.7: Cobalt minerals.

Mineral	Cobalt content, %
Cattierite, CoS_2 (pure)	47.8
Linnærite, Co_3S_4 (pure)	58.0
Siegenite, $(\text{Co},\text{Ni})_3\text{S}_4$	20.4–26.0
Carrollite, $(\text{Co}_2\text{Cu})\text{S}_4$	35.2–36.0
Cobaltite, $(\text{Co},\text{Fe})\text{AsS}$	26.0–32.4
Safflorite, $(\text{Co},\text{Fe})\text{As}_2$	13.0–18.6
Smaltite, $(\text{Ca},\text{Ni})\text{As}_2$	ca. 21
Glauco-dot, $(\text{Co},\text{Fe})\text{AsS}$	12.0–31.6
Skutterudite, $(\text{Co},\text{Fe})\text{As}_3$	10.9–20.9
Heterogenite, $\text{CoO}(\text{OH})$ (pure)	64.1
Asbolite	0.5–5.0
Erythrite, $(\text{CoNi})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	18.7–26.3
Gersdorffite, $(\text{Ni},\text{Co})\text{AsS}$	(low)
Pyrrhotite, $(\text{Fe},\text{Ni},\text{Co})_{2-1}\text{S}_2$	up to 1.00
Pentlandite, $(\text{Fe},\text{Ni},\text{Co})_9\text{S}_8$	up to 1.50
Pyrite, $(\text{Fe},\text{Ni},\text{Co})\text{S}_2$	up to 13.00
Sphalerite, $\text{Zn}(\text{Co})\text{S}$	up to 0.30
Arsenopyrite, $\text{Fe}(\text{Co})\text{AsS}$	up to 0.38
Manganese oxide minerals	0.10–1.0

Ore Deposits. Cobalt is produced mainly as a by-product of the mining and processing of the ores of other metals, particularly those of copper, nickel, and silver, but also those of gold, lead, and zinc.

The deposits of cobalt can be classified under the following headings:

- **Hypogene deposits** associated with mafic intrusive igneous rocks. The massive and disseminated iron-nickel-copper sulfides containing cobalt are important examples

of this type of deposit. They include the ore from the Sudbury district of Ontario, which has an average cobalt content of 0.07%. The suite of ore minerals consists of pyrrhotite, pentlandite, pyrite, marcasite, cobaltite, and gersdorffite in veins stringers and disseminated grains within an igneous host rock of Precambrian age.

- **Contact metamorphic deposits** associated with mafic rocks. Deposits of magnetite, chalcopyrite, and cobalt-containing pyrite, formed by contact metamorphism of carbonate rock by sills and dikes of diabase, gave the ore deposits at Cornwall and Morgantown in the United States.
- **Lateritic Deposits.** The weathering of peridotite and serpentine generally gives laterite that is rich in iron, nickel, cobalt, and chromium. Commercially valuable deposits contain 40–50% iron, 1–2% nickel, and 0.01–0.1% cobalt. Major lateritic deposits occur in Cuba, New Caledonia, Australia, the United States, and Russia.
- **Massive sulfide deposits** in metamorphic rocks, largely of volcanic sedimentary origin. These deposits consist mainly of pyrite and pyrrhotite and are mined in the United States.
- **Hydrothermal deposits** are subdivided into two classes: vein deposits and replacement deposits. Some of these deposits are the only ones that have been mined specifically as sources of cobalt. In Canada, veins that contain as much as 10% cobalt occur in the Cobalt-Gowganda region of Ontario, whereas veins in the Bou-Azzer area of Morocco contain an average of 1.2% cobalt. Hydrothermal replacement deposits containing 0.5% cobalt as gersdorffite are found in Burma and at Outokumpu in Finland; a copper-rich sulfide deposit contains 0.2% cobalt mainly in linnæite.
- **Strata-bound deposits:** the copper-cobalt deposits of Zaire and Zambia are of this type. They occur in folded shale and dolomite and contain a number of minerals, including chalcopyrite, bornite, chalcocite, linnæite, and carrollite. The ore bed is 6–24

m thick and currently provides the world's major source of cobalt.

- **Deposits formed as chemical precipitates** usually contain chemically precipitated cobalt in associated marine manganese nodules.

Reserves. As generally accepted, there are $3\text{--}5 \times 10^6$ t of minable cobalt reserves and a further $4\text{--}5 \times 10^6$ t of potential reserves, Table 18.8 lists the reported reserves in a number of countries. However, the minable reserves do not have the same degree of profitability. Cuba has minable resources of cobalt, but provides only 5% of the world production because its ore bodies are laterites with only small quantities of nickel and cobalt that are costly to refine. Zaire produces more than half of the world's cobalt because its ores can be treated more profitably.

In addition to the land-based reserves listed in Table 18.8, almost 6×10^9 t of copper is available in marine nodules if it can be recovered and worked economically.

Table 18.8: Cobalt reserves.

Country	Reserves, $\times 10^3$ t	Country	Reserves, $\times 10^3$ t
Australia	295	New Caledonia	385
Brazil	> 9	New Guinea	18
Burma	16	Philippines	159
Canada	250	Puerto Rico	68
Colombia	22.5	Solomon Islands	22.5
Cuba	1 048.5	Soviet Union	181.5
Dominican Republic	89	Uganda	8
Finland	22.5	United States	> 764
Guatemala	45.5	Venezuela	60
Japan	2.5	Zaire	1 920
		Zambia	370

18.5 Production

18.5.1 Concentration of the Ores

[1, 2, 9]

The first stages of the production of cobalt from its ores involve the separation of cobalt-bearing minerals from the gangue and from minerals containing other desirable metals but not cobalt. The concentrates obtained by applying physical separation methods such as gravity separation or froth flotation to ores can

increase the cobalt content to 10–15% from cobalt-rich ores. However, in general, these processes only increase the level of cobalt from 0.1–0.6% in ores to a few percent. The concentration procedures for the main types of ores are described in this section.

Arsenide Ores. Cobalt arsenide minerals have specific gravities of 6.5–7.2 g/cm³ and can be separated at relatively large grain size by gravity methods. Concentrates containing 13–14% cobalt have been produced by these methods from Moroccan ores at Bou-Azzer containing 2% cobalt.

Sulfoarsenide Ores. The main mineral in this type of ore, cobaltite, can be effectively separated by froth flotation with xanthate at pH 4–5, although iron sulfide minerals are also floated under similar conditions and must be separated from the cobalt concentrate.

Sulfide Ores. The chalcocite and carrollite fractions of the ores of the Shaba province in Zaire are floated together at pH 9.2 by using lime, xanthates as collectors, and triethoxybutane as the frothing agent to give a concentrate containing 43–53% copper and 0.5–3% cobalt. The copper cobalt sulfide ores of Zambia are first treated to float the copper minerals selectively at pH 10.5–11; at this stage the presence of sodium cyanide depresses the cobalt minerals. These are subsequently activated by sulfuric acid and floated at pH 8.5–9 with sodium isopropyl xanthate; the concentrates contain up to 3.5% cobalt. The flotation process at the Outokumpu Keretti Mill first separates the copper minerals with xanthates at pH 11–11.5 in the presence of lime and sodium cyanide. The cobalt minerals are then floated at pH 9 to recover 65–75% of the cobalt from an ore containing 0.23–0.31% cobalt; the concentrate contains 0.7–0.82% cobalt. The nickel–copper–cobalt sulfide ores of Ontario are first treated to separate the sulfide minerals from gangue, and the cobalt minerals are then contained in the nickel sulfide concentrate.

Oxide Ores. Two methods have been used on a commercial scale to float oxide ores. The *palm oil process* collects the concentrate in a

3:1 mixture of hydrolyzed palm oil and gas oil emulsified in carbonated hot water; this process can give concentrates containing 23–25% copper and 2–3% cobalt, representing a cobalt recovery of 50–70% from the ore. The *sulfidization process* is used for mixed oxide–sulfide ores to float sulfide ores first and to concentrate oxide minerals subsequently in a xanthate flotation.

18.5.2 Extraction [1, 2, 9]

Cobalt can be extracted from concentrates and occasionally directly from the ore itself by hydrometallurgical, pyrometallurgical, and electrometallurgical processes. Although most methods of extraction are based on hydrometallurgy, cobalt concentrates, mattes, and alloys have been reduced to metal by pyrometallurgical methods. Most arsenic-free cobalt concentrates can, for example, be mixed with lime and coal and melted in a reducing atmosphere to give cobalt–copper–iron alloys. Two types of alloys are obtained, a *white alloy* containing ca. 40% cobalt that is processed for cobalt and a *red alloy* containing ca. 4% cobalt that is processed for copper. Recovery of copper from the red alloy produces a cobalt-rich slag that can be recycled with the ores. The hydrometallurgical processes involve (1) leaching of concentrates to give a cobalt-containing solution, (2) separation of cobalt from the other metal ions in solution, and (3) reduction of cobalt ions to metal. Electrometallurgical processes are used in the electrowinning of the metal from leach solutions and in refining the cobalt that has been extracted by hydrometallurgical or pyrometallurgical methods.

18.5.2.1 Leaching of Cobalt Ores and Concentrates

Cobalt can be leached from its ores and concentrates in both acidic and alkaline media. Processes involving acid–sulfate leaching include (1) treatment of oxide ore concentrates with sulfuric acid containing a reducing agent, (2) extraction of cobalt sulfate from sulfide ores following an oxidizing roast, (3) extrac-

tion following a sulfatizing roast, and (4) extraction by pressure leaching with sulfuric acid, often in the presence of oxygen; the *Chemico process* for the treatment of arsenic-containing ores is, for example, based on an acid pressure leach. Acid leaching processes based on hydrochloric acid extraction and chloridation roasting have also been used.

Processes that involve the extraction of cobalt into alkaline solutions depend on the formation of the hexamminocobalt(II) species $[\text{Co}(\text{NH}_3)_6]^{2+}$, which remains in solution for long periods because of its kinetic stability, even though it has low thermodynamic stability. Ammoniacal leaching has been successfully applied to ores after a reducing roast, and the Sherritt Gordon process depends on ammonia solution pressure leaching.

Cobalt from Copper–Cobalt Concentrates. The copper–cobalt ores of Zaire and Zambia are treated by a sulfatizing roast in a fluidized-bed furnace to convert copper and cobalt sulfides into soluble oxides and iron into insoluble hematite. The calcine is subsequently leached with sulfuric acid from the spent copper recovery electrolyte. Oxide concentrates are introduced at this leaching step to maintain the acid balance in the circuit. Iron and aluminum are removed from the leach solution, and copper is electrowon on copper cathodes. A part of the spent electrolyte enters the cobalt recovery circuit and is purified by removal of iron, copper, nickel, and zinc prior to precipitation of cobalt as its hydroxide. In the final stages, this cobalt hydroxide is redissolved and the metal is refined by electrolysis and by degassing to remove any traces of hydrogen. Figure 18.1 shows the flow diagram of the process used at the Générale des carrières et des mines (Gécamines) plant in Luilu.

Cobalt from Nickel Sulfide Concentrates. Nickel sulfide concentrates can be treated by either roasting or flash smelting to give a matte from which nickel and cobalt can be recovered hydrometallurgically, or they may be treated directly by an ammonia solution pressure leach. In the *Sherritt Gordon process* used at Fort Saskatchewan in Canada, which is

illustrated as a flow diagram in Figure 18.2, a feed of matte and sulfide concentrate, containing about 10% nickel, 2% copper, 0.4% cobalt, 33% iron, and 30% sulfur, is pressure leached in autoclaves at 83 °C and 0.7 MPa (7 bar) with an ammoniacal medium. This converts most of the sulfide via thiosulfate and polythionate to sulfate and solubilizes nickel, copper, and cobalt as ammine complexes. Most of the copper in the leach solution is precipitated as copper sulfides when the solution is distilled to recycle ammonia. The solution is treated with hydrogen sulfide to remove any residual copper, and any sulfide or sulfamate remaining at this stage is converted to sulfate by a pressure oxidation hydrolysis reaction at 6.5 MPa (65 bar). The solution then enters reduction autoclaves, where nickel powder is precipitated by reduction with hydrogen at 3.6 MPa (36 bar). The remaining solution, which contains 1–1.5 g/L of both cobalt and nickel, is treated in an autoclave with hydrogen sulfide to precipitate cobalt and nickel sulfides, which are subsequently leached with sulfuric acid at 140 °C and 6.4 MPa (64 bar). Iron is removed from this leach liquid at pH 2.5–3.0 by addition of ammonia solution. The cobalt(II) in solution is oxidized in air to give a very soluble cobalt(III) pentammine complex. Nickel is subsequently precipitated from the solution in two steps as a nickel ammonium sulfate. Cobalt powder is then added along with sulfuric acid to reduce the cobalt(III) pentammine complex to cobalt(II), which is finally reduced to cobalt powder by treatment with hydrogen at 120 °C and 4.6 MPa (46 bar).

Cobalt-containing mattes and mixed sulfide concentrates have also been treated by pressure leaching with sulfuric acid, for example, at Amax at Port Nickel in the United States, MRR in South Africa, Nippon Mining and Sumitomo Metals Mining Co. in Japan, and Outokumpu Oy in Finland. The flow diagram for the Outokumpu Kukkola plant (Figure 18.3) is used to illustrate this type of cobalt recovery process. Two companies, Falconbridge in Canada and Norway and Société le Nickel in France, leach nickel mattes and sulfide con-

concentrates in chloride media at ambient pressure.

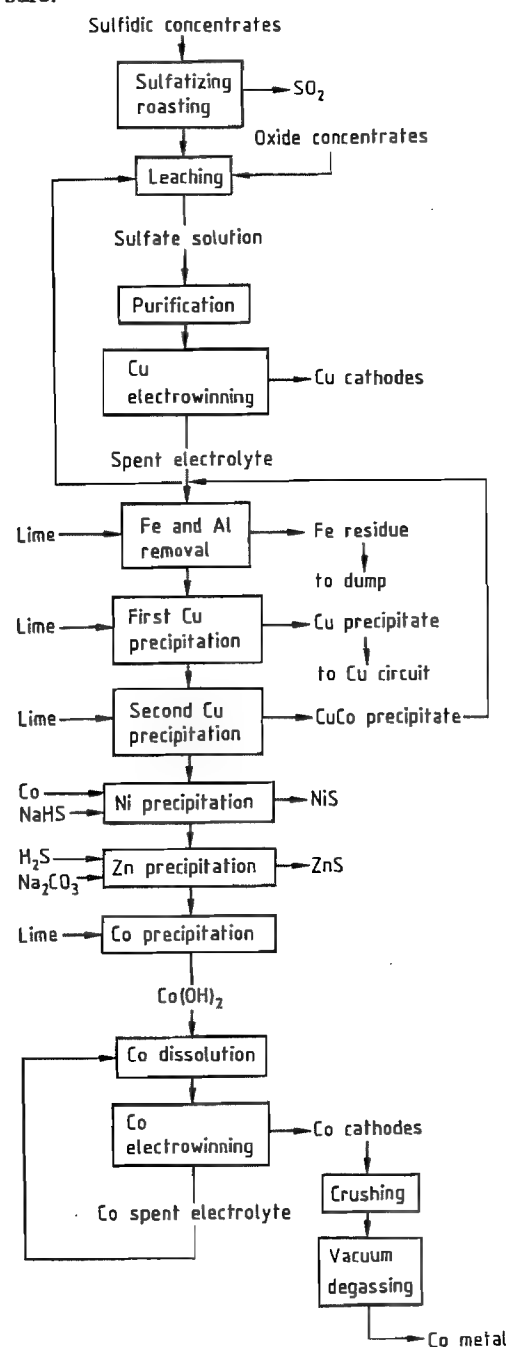


Figure 18.1: Flow diagram of the Gécamines process.

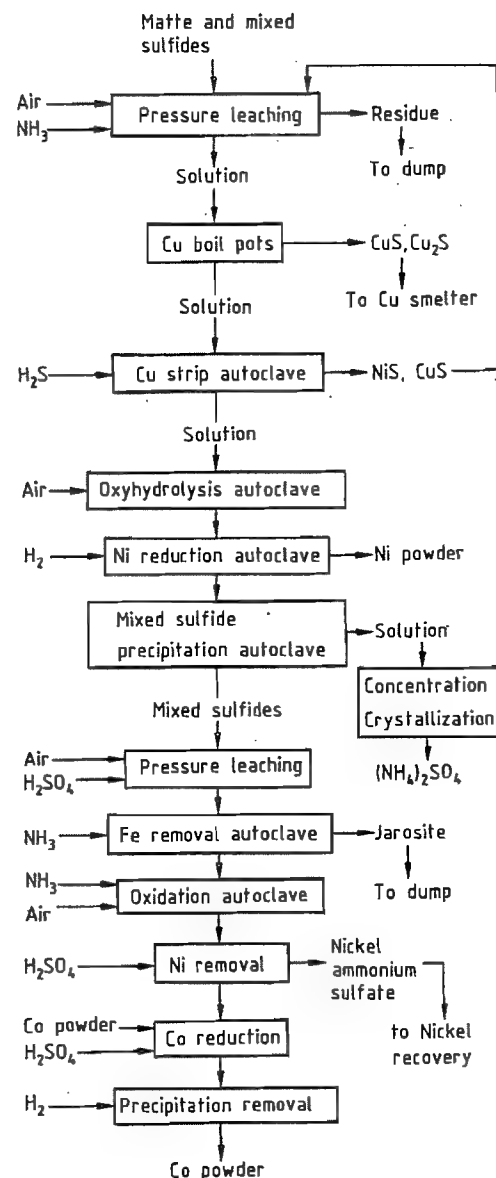


Figure 18.2: Flow diagram of the Sherritt Gordon process.

Falconbridge use a hydrochloric acid leach at 70 °C for about 15% of their feed and a direct chlorine leach for the remainder. The leach medium used by Société le Nickel is chlorine in iron(III) chloride. At the INCO Copper Cliff plant nickel-copper mattes are

cooled slowly and crushed prior to magnetic separation, which isolates a nickel-copper-cobalt alloy. The alloy is smelted in a top-blown rotary converter, desulfurized by oxygen lancing, and granulated. Nickel is volatilized from the granules as Ni(CO)_4 by the INCO carbonyl process to give a residue from which cobalt can be leached; the solution obtained allows cobalt to be electrowon after some purification steps.

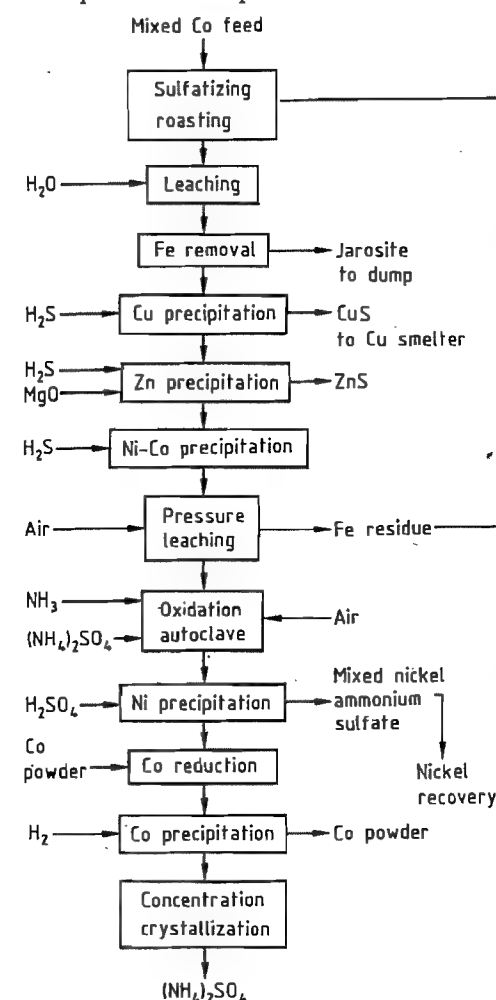


Figure 18.3: Flow diagram of the Outokumpu process.

Cobalt from Laterite Ores. Laterite ores can be treated by the methods described above for nickel mattes after a calcining preroast.

Greenvale Mines in Queensland (Australia) have developed a new process for laterite ore treatment. The ground ore is mixed with 40% of fuel oil and roasted in Herreshoff furnaces with 17 overlapping heating elements. As the ore falls down the furnace through increasingly hotter zones in a reducing atmosphere, the ore is finally reduced to metal at 750 °C in an oxygen-free atmosphere. The roasted ore is leached with an ammonia-ammonium carbonate solution to solubilize the nickel and cobalt as ammine complexes. The leach solution is then purified by removing iron as the hydroxide prior to precipitation of cobalt and part of the nickel as sulfides with hydrogen sulfide. The cobalt-rich sulfide is calcined to provide a material from which cobalt can be extracted.

Cobalt from Arsenide Ores. Arsenic-containing concentrates are roasted in a fluidized bed at 600–700 °C to remove 60–70% of the arsenic present as arsenic(III) oxide. The roasted ores can be treated with hydrochloric acid and chlorine or with sulfuric acid to give a leach solution that can be purified by hydrometallurgical methods and from which cobalt can be recovered by electrolysis or by carbonate precipitation.

18.5.2.2 Separation of Cobalt from Other Metal Ions in Leach Solutions

A major part of cobalt recovery from leach solutions is concerned with its separation from other elements. Because of the similarities in chemical behavior of cobalt and nickel, the separation of these two elements has been studied extensively and is well-known. This section deals with chemical methods of separation of cobalt from nickel and with physico-chemical methods of separation of cobalt from other elements.

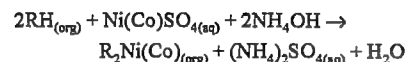
Chemical Methods of Separation. The chemical methods of separating cobalt from other metals use the different solubilities and kinetic or thermodynamic stabilities of their compounds. The most important compounds that have been used in separation are hydroxides, carbonates, ammine complexes, double

ammonium sulfates, sulfides, chlorides, and carbonyls; the cementation to metal is also utilized. For examples, see Section 18.5.2.1. The relative solubilities of cobalt(III) and nickel(II) hydroxides in the presence and absence of complexing agents and of cobalt(II) and nickel(II) carbonates in solutions containing NH_3 and CO_2 have also been used to separate these elements. Fractional crystallization of chloride-containing media can be used to concentrate cobalt in solution and nickel in solid nickel chloride dihydrate.

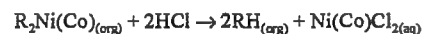
Physical Methods of Separation. Many physical methods have been used to separate cobalt from other elements, but the three most important are electrolysis, solvent extraction, and ion exchange.

In most solvent extraction processes, cobalt is extracted with a tertiary amine from chloride solutions although cobalt and nickel can be separated from each other with phosphate or carboxylic acid reagents from ammoniacal sulfate solutions. In the sulfuric acid leach process of Nippon Mining at Hitachi, solvent extraction is used to extract zinc from the leach solution with di-(2-ethylhexyl) phosphonic acid (DEHPA) at pH 2–3 prior to solvent extraction of cobalt with an alkylphosphonic acid. The Falconbridge and Société le Nickel processes both involve solvent extraction of cobalt from chloride solution with trioctylamine. The Sumitomo Metals Mining Co. uses a solvent extraction process to coextract cobalt and nickel with versatic acid. The extract is then stripped with hydrochloric acid and cobalt is reextracted from the chloride solution with tri-*n*-octylamine to give an extract from which cobalt is stripped and electrowon. The flow diagram for this process is shown in Figure 18.4, and the solvent extraction process can be expressed in terms of the following chemical equations:

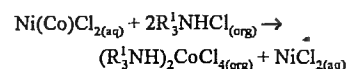
Extraction:



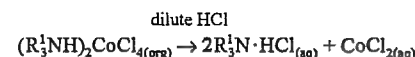
Stripping:



Extraction:



Stripping:



where RH is versatic acid in kerosene and R_3^1N is tri-*n*-octylamine in xylene; (org) and (aq) are organic and aqueous phases, respectively.

18.5.2.3 Electrowinning [9]

Cobalt can be extracted and obtained as high-purity metal by electrolysis of sulfate or chloride solutions. Solutions of pH 1–4 are necessary for the electrowinning of cobalt, and the pH is often maintained by suspending cobalt hydroxide or cobalt carbonate in the electrolyte to use up the acid produced at the anode. Current densities of 5 A/dm² are used with current consumptions of ca. 6.5 kWh per kilogram of cobalt. Electrolytically refined cobalt is usually purer than 99.5%.

18.6 Cobalt Powders [11–13]

18.6.1 Production

Cobalt powder can be produced by a number of methods, but those of industrial importance involve the reduction of oxides, the pyrolysis of carboxylates, and the reduction of cobalt ions in aqueous solution with hydrogen under pressure. Very pure cobalt powder is prepared by the decomposition of cobalt carbonyls.

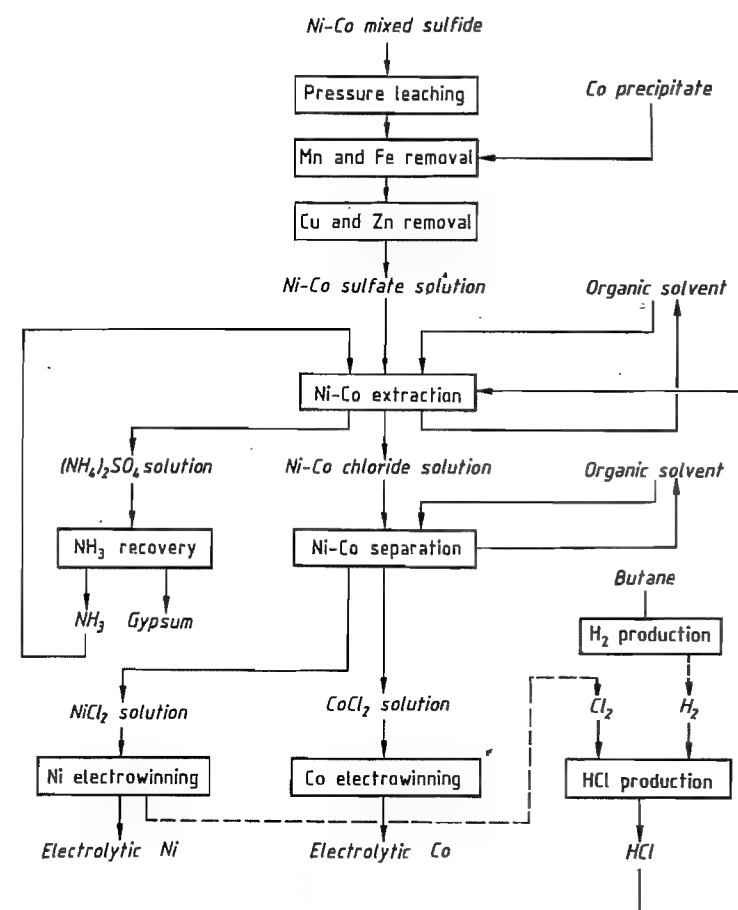


Figure 18.4: Flow diagram of the Sumitomo process.

Reduction of Oxides. Grey cobalt(II) oxide (CoO) or black cobalt(II) cobalt(III) oxide (Co_3O_4) is reduced to metal powder with carbon monoxide or hydrogen. The reactions occur under conditions well below the melting point of the oxides or the metal. The purity of the powder obtained is 99.5% with a particle size of ca. 4 μm , although the density and the particle size of the final product depend on the reduction conditions and on the particle size of the parent oxide. The finely powdered metal is stored at very low temperature.

Pyrolysis of Carboxylates. The thermal decomposition of such cobalt carboxylates as formate or oxalate in a controlled reducing or neutral atmosphere produces a high-purity

(about 99.9%), light, malleable cobalt powder with a particle size of ca. 1 μm that is particularly suitable for the manufacture of cemented carbides. The particle size, form, and porosity of the powder grains can be changed by altering the pyrolysis conditions.

Reduction of Cobalt Ions in Solution. Purified leach solutions containing cobalt pentammine complex ions can be treated in autoclaves with hydrogen under pressure and at high temperature to give an irregular chain-like form of the powder that is suitable for consolidation by direct strip rolling.

18.6.2 Uses

18.6.2.1 Cemented Carbides

One of the most important uses of metallic cobalt is as a bonding agent in cemented carbides [14, 15] that are used extensively as cutting tools for metals, rocks, and other high-strength materials. No suitable substitute has been found for cobalt as a cementing agent for carbides. The most commonly used cemented carbide, tungsten carbide containing 2–30% cobalt, is manufactured as follows: pure cobalt powder is added to tungsten carbide (particle size ca. 1 μm), and the mixture is ball-milled for a long period by using hard metal balls. The mixed powders are then consolidated by cold pressing, by hot pressing at ca. 1300–1400 °C, by cold extension, or by slip casting to produce small artifacts, large artifacts, constant-section rods, and complex-shaped articles, respectively. The consolidated parts are sintered in a reducing atmosphere at 1300–1600 °C. The sintering process involves the formation of a liquid phase; the cobalt liquefies at ca. 1320 °C and dissolves tungsten and carbon from the carbide. When the mixture is cooled, most of the tungsten and carbon reprecipitates, but the binder phase is much stronger than pure cobalt because enough tungsten and carbon are present to stabilize the metal in its cubic form. During the sintering process, the consolidated powders shrink by 20%. The binding mechanism depends on (1) the liquid metal phase to wet the carbide particles so that surface tension forces help densify the sintered phases and (2) on the ability of the liquid to dissolve and retain traces of carbide impurities.

The properties of cemented carbides are controlled by the amount of cobalt present and the particle size of the carbide used. The hardness of the cemented carbides increases with decreasing particle size and with increasing cobalt content. The impact strength of cemented carbides is directly proportional to the cobalt content it rises from less than 1 kgm for a sample with 6% cobalt to ca. 2.5 kgm for a sample with 25% cobalt in tungsten carbide

with a particle size of 1.4–3.1 μm . The properties of cemented tungsten carbides can be improved by the addition of other carbides such as those of niobium, tantalum, or titanium.

18.6.2.2 Cobalt Powders in Powder Metallurgy and Cobalt-containing Metal [15]

Cobalt powders have been used in the formation of a number of alloy phases including maraging steel by hot extension of prealloyed powders, cobalt-based superalloys by consolidation of powders involving liquid phase sintering, fine-particle magnetic alloys, and bearing materials impregnated with low-friction substances such as graphite, lead, nylon, and molybdenum disulfide.

18.7 Alloys [1–3, 9]

About 64% of the cobalt is consumed in alloy compositions. The most important cobalt alloys are discussed in this article under the following headings:

- High-temperature alloys
- Magnetic alloys
- Hard metal alloys
- Cobalt-containing high-strength steels
- Electrodeposited alloys
- Alloys with special properties

18.8 Compounds [17]

18.8.1 Chemical Properties of Cobalt

Cobalt is much less reactive than iron. It is stable to atmospheric oxygen unless heated. When heated, it is first oxidized to Co_3O_4 and then, above 900 °C, to CoO , which is also the product of the reaction between the red-hot metal and steam. The activation energy of the oxidation above 900 °C has been calculated as 155–160 kJ/mol. The metal does not combine directly with hydrogen or nitrogen, but it combines with carbon, phosphorus, and sulfur on

heating. The reaction with sulfur is influenced by the formation of a low melting eutectic (877 °C) between the metal and the Co_4S_3 phase; the reaction between cobalt and sulfur is rapid above this temperature. Below 877 °C, a protective layer of sulfide scale is formed. In an atmosphere of hydrogen sulfide, cobalt also forms a scale of sulfide, but in air containing sulfur dioxide, a mixed oxide sulfide scale is formed.

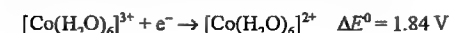
In bulk form, cobalt is resistant to many mild corrosive agents, but it is more readily attacked when it is finely divided. Table 18.9 gives the corrosion rates of cobalt in some aqueous media. Cobalt is strongly attacked by concentrated nitric acid at ambient temperature. The metal dissolves slowly in dilute mineral acids, the Co^{2+}/Co potential being -0.277 V.

Table 18.9: Corrosion of cobalt in aqueous media at 25 °C.

Corrosive medium	Rate of cobalt corrosion, $\text{mgdm}^{-2}\text{d}^{-1}$
Distilled water	1.1
5 vol% Ammonia	5.3
10 vol% Sodium hydroxide	5.6
Conc. phosphoric acid	7.4
50% Phosphoric acid (aqueous)	65.1
5 vol% Acetic acid	12.5
5 vol% Sulfuric acid	56.8
50% Hydrofluoric acid (aqueous)	178.6

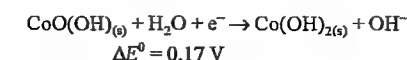
The solubility of oxygen in cobalt is 0.006, 0.013, 0.125, and 0.4% (at 600, 1200, 1510, and 1700 °C, respectively). Nitrogen is only slightly soluble (40 mg/kg) in cobalt at its melting point; the solubility rises to 60–70 mg/kg at 1750 °C. The solubility of hydrogen in cobalt increases with temperature from 1 mg/kg at 700 °C to ca. 8 mg/kg at the melting point. The solubility of hydrogen in the liquid metal increases to ca. 20 mg/kg at 1500 °C and to ca. 27 mg/kg at 1750 °C.

The main oxidation states of cobalt are Co^{2+} and Co^{3+} . In acid solution and in the absence of complexing agents, Co^{2+} is the stable oxidation state, with oxidation to Co^{3+} being difficult.



The oxidation can be achieved by electrolysis or ozone, but the Co^{3+} is very unstable and rapidly reduced to Co^{2+} , even at room temperature, with evolution of oxygen from the water. The solution chemistry of cobalt in acid solution in the absence of complexing agents is dominated by Co^{2+} . The most common species present is $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, although the ions $[\text{CoX}_3]^-$, $[\text{CoX}_4]^{2-}$, and $[\text{CoX}_6]^{4-}$ ($\text{X} = \text{halide}$) are also found in solutions of hydrogen halides. Cobalt is often removed from solution as its sulfide, and it is interesting to note that although the precipitates of cobalt sulfide obtained by using H_2S are not readily soluble in dilute acids, those obtained by using Na_2S or $(\text{NH}_4)_2\text{S}$ are soluble. All sulfide precipitates become less soluble as they age in the atmosphere to form $\text{Co}(\text{OH})\text{S}$. The cobalt dihalides (except fluoride) are also readily soluble in some organic solvents such as alcohol, acetone, and methyl acetate.

In alkali, Co^{2+} is more readily oxidized to Co^{3+} :



In the presence of complexing agents, oxidation is very easy in any solution because Co^{3+} has a particularly high affinity for complex formation. With N-donor ligands the redox reaction in the presence of ammonia is:



Table 18.10: ΔE^0 for some $\text{Co}^{3+}/\text{Co}^{2+}$ couples in acid solution.

Redox reaction	ΔE^0
$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-} + e^- \rightleftharpoons [\text{Co}(\text{C}_2\text{O}_4)_3]^{4-}$	0.57
$[\text{Co}(\text{EDTA})]^- + e^- \rightleftharpoons [\text{Co}(\text{EDTA})]^{2-}$	0.37
$[\text{Co}(\text{bipy})_3]^{3+} + e^- \rightleftharpoons [\text{Co}(\text{bipy})_3]^{2+}$	0.31
$[\text{Co}(\text{en})_3]^{3+} + e^- \rightleftharpoons [\text{Co}(\text{en})_3]^{2+}$	0.18
$[\text{Co}(\text{CN})_6]^{3-} + \text{H}_2\text{O} + e^- \rightleftharpoons [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} + \text{CN}^-$	-0.8

Oxidation of Co^{2+} solutions containing complexing agents can be achieved with air or hydrogen peroxide. Thus, the solution chemistry of cobalt in the presence of complexing agents is dominated by the complex chemistry of Co^{3+} . The sensitivity of the reduction potential of the $\text{Co}^{3+}/\text{Co}^{2+}$ couple to different ligands whose presence renders Co^{2+} unstable

to air oxidation is shown by the data in Table 18.10.

Cobalt(II) Compounds. Cobalt combines with oxygen to form cobalt(II) oxide, CoO , which is stable above 900 °C. This oxide has the sodium chloride structure and is antiferromagnetic at ordinary temperature. When cobalt(II) oxide is heated at 400–500 °C in an atmosphere of oxygen, the cobalt(II,III) oxide, Co_2O_3 , is formed. This mixed-valence oxide has the spinel structure with cobalt(II) in tetrahedral sites and cobalt(III) in octahedral sites. Cobalt hydroxide, $\text{Co}(\text{OH})_2$, is a product of the hydrolysis of solutions containing Co^{2+} ions. The hydroxide is amphoteric, dissolving both in alkali, to give blue solutions containing the $[\text{Co}(\text{OH})_4]^{2-}$ ion, and in acids. Cobalt(II) forms an extensive range of simple and hydrated salts with all of the common anions including acetate, bromide, carbonate, chloride, fluoride, nitrate, perchlorate, and sulfate. Many of the hydrated salts and their solutions contain the pink octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion. Although complexes of cobalt(II) are generally unstable to oxidation, a number of octahedral species are formed, including (1) a series of $[\text{Co}(\text{N}-\text{N})_3]^{2+}$ complexes with neutral bidentate donor ligands, such as ethylenediamine and bipyridyl, and (2) the acetylacetonates $[\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}]$ and $\text{Co}(\text{acac})_2$. Tetrahedral complexes $[\text{CoX}_4]^{2-}$ are usually formed with monodentate anionic ligands, such as chloride, bromide, iodide, thiocyanate, azide, and hydroxyl. Tetrahedral $[\text{CoX}_2\text{L}_2]$ complexes are formed by a combination of two such ligands with two neutral ligands (L). Addition of cyanide to a solution of Co^{2+} produces a dark green color attributed to the $[\text{Co}(\text{CN})_5]^{3-}$ ion.

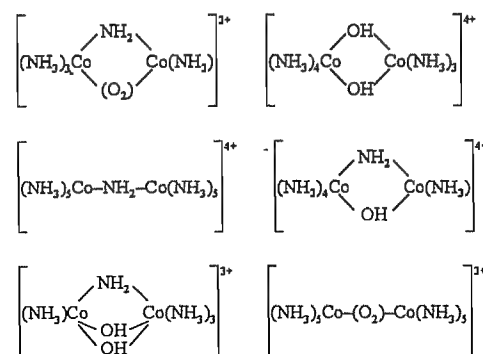
The colors produced by cobalt(II) complexes in aqueous media have been used to distinguish between octahedral and tetrahedral coordination in the complexes. In general, octahedral species are pink to violet, whereas tetrahedral species are blue. This is not an infallible distinction, but it does provide a use-

ful guide that can be improved by analyzing the electronic spectra of the complexes.

Cobalt(III) Compounds. In addition to the mixed-valence oxide Co_2O_3 , impure forms of the unstable cobalt(III) oxide, Co_2O_3 , have been prepared. Very few simple cobalt(III) salts are known. The blue sulfate, $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, which contains the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ species, can be obtained by the electrolytic oxidation of cobalt(II) in 4 M sulfuric acid solution. It is stable when dry, but decomposes in the presence of moisture. The alums $\text{MCo}(\text{III})(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (M = K, Rb, Cs, NH_4) are also known, and a hydrated fluoride $2\text{CoF}_3 \cdot 7\text{H}_2\text{O}$ has been reported.

The chemistry of cobalt(III) is dominated by complex formation. Cobalt(III) complexes are kinetically inert, and for this reason, indirect methods of syntheses are used to obtain them. Usually the ligand is added to a solution of Co^{2+} , which is then oxidized with some convenient oxidant, often in the presence of a catalyst such as activated charcoal. A wide range of cobaltamines have been prepared and studied; the species identified in solution or as solid derivatives include $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ (X = Cl, Br, NO_2 , NO_3), and *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4\text{X}_2]^{+}$ (X = Cl, NO_2).

In addition to these simple cobaltamines, a number of polynuclear species containing bridging groups such as NH_2 , NH_2^- , NO_2 , OH^- , and O_2 have been prepared. Polynuclear cobaltamines that have been identified include:



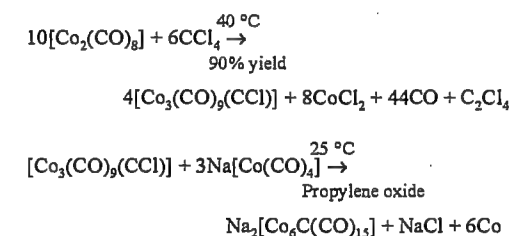
Complexes of cobalt(III) with O-donor ligands are generally less stable than those with N-donor species, although $[\text{Co}(\text{acac})_3]$ and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ are known. Apart from the O_2 -bridged compounds mentioned above, the octahedral fluoro complexes $[\text{CoF}_6]^{3-}$ and $[\text{CoF}_3(\text{H}_2\text{O})_3]$ are the only known high-spin cobalt(III) complexes, the paramagnetic moment of $[\text{CoF}_6]^{3-}$ at room temperature being about 5.8 BM. All other cobalt(III) complexes are low-spin and diamagnetic, including the hexacyanocobaltates(III), $[\text{Co}(\text{CN})_6]^{3-}$, and the hexanitritocobaltates(III), $[\text{Co}(\text{NO}_2)_6]^{3-}$.

In addition to the two most stable oxidation states, 2+ and 3+, cobalt also forms compounds in the 1-, 0, 1+, and 4+ oxidation states. There are only a few reported examples of Co(IV) compounds, mainly fluoro complexes, CoF_6^{2-} , and mixed-metal oxides (the purity of compounds in this oxidation state is questionable).

The formation of cobalt compounds in oxidation states lower than 2+ requires the presence of stabilizing π -acceptor ligands. The 1+ state is not common for cobalt, and most of the known examples are pentacoordinated complexes of the type $[\text{Co}(\text{NCR})_5]^+$ (NCR = organic nitrile). Cobalt forms a wide range of complexes in which its formal oxidation state is 0 or 1-. Many of these contain ligands such as CO, CN^- , NO^+ , and RNC , but other ligands such as tertiary phosphanes also stabilize lower oxidation states to give compounds like $[\text{Co}(\text{P}(\text{CH}_3)_3)_4]^+$, which is prepared by reducing an ethereal solution of cobalt(II) chloride with sodium or magnesium amalgam in the presence of trimethylphosphane.

Cobalt Carbonyls [17, 18]. The carbonyl complexes of cobalt are important because of their uses as hydroformylation catalysts. Because cobalt has an odd number of valence electrons, it can satisfy only the eighteen-electron rule in its carbonyls if Co-Co bonds are formed. For this reason, the principal binary carbonyls of the element are octacarbonyldicobalt, $[\text{Co}_2(\text{CO})_8]$, dodecacarbonyltetracobalt, $[\text{Co}_4(\text{CO})_{12}]$, and hexadecacarbonylhexas-cobalt, $[\text{Co}_6(\text{CO})_{16}]$.

Octacarbonyldicobalt is prepared by heating the metal to 250–300 °C at 200–300 bar of carbon monoxide or by heating cobalt carbonate under similar conditions in the presence of hydrogen. It is an air-sensitive orange-red solid with a melting point of 51 °C. The compound can be reduced with sodium amalgam in benzene to give the tetrahedral monomeric ion $[\text{Co}(\text{CO})_4]^-$, acidification of which leads to tetracarbonylhydridocobalt, $[\text{HCo}(\text{CO})_4]$. This hydride is a yellow liquid that forms a colorless vapor. It melts at -26 °C and decomposes above this temperature to H_2 and $[\text{Co}_2(\text{CO})_8]$. It is partly soluble in water to give a strong acid solution containing $[\text{Co}(\text{CO})_4]^-$ ions. The hydrogen atom in $[\text{HCo}(\text{CO})_4]$ is bound directly to the cobalt, giving a Co-H infrared stretching frequency of ca. 1934 cm^{-1} . The $[\text{Co}(\text{CO})_4]^-$ ion is reoxidized to $[\text{Co}_2(\text{CO})_8]$ by carbon tetrachloride, and further reaction with this reagent leads to a triply bridged chloromethynyl derivative, from which a carbidocarbonyl compound, disodium carbidopentadecacarbonylhexas-cobaltate, $\text{Na}_2[\text{Co}_6\text{C}(\text{CO})_{15}]$, can be obtained:



Other carbidocarbonyls are obtained by similar routes, including $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$, $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$, and $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}\text{H}]^{4-}$. Dodecacarbonyltetracobalt is obtained as a green black solid by heating $[\text{Co}_2(\text{CO})_8]$ in an inert atmosphere at 50 °C.

The structure of $[\text{Co}_2(\text{CO})_8]$ in the solid state is different from that in solution. The solid-state structure shown in Figure 18.5A involves two bridging carbonyl groups and can be best rationalized in terms of the formation of a bent Co-Co bond. In solution, however, this structure is in equilibrium with the form shown in Figure 18.5B, in which the dimer is held together by a Co-Co bond. The structure

of $[\text{Co}_4(\text{CO})_{12}]$ is shown in Figure 18.5C. The structure of the carbidocarbonyl (Figure 18.5D) shows the presence of a carbon atom at the center of a distorted square antiprismatic cobalt cluster.

In addition to the carbonyls, cobalt also forms complexes with N_2 and NO^+ , which are isoelectronic with CO. Examples of this type of complex are $[\text{CoH}(\text{PR}_3)_3(\text{N}_2)]$ and $[\text{Co}(\text{CO})_3\text{NO}]$, where R is an alkyl group.

18.8.2 Commercially Important Cobalt Compounds [19]

Table 18.11 lists the known applications of cobalt compounds. The most important commercially available compounds are the oxides, as well as hydroxide, chloride, sulfate, nitrate, phosphate, carbonate, acetate, oxalate, and other carboxylic acid derivatives.

Cobalt Oxides. Two main types of cobalt oxide distinguishable by their colors are available: *grey* cobalt(II) oxide, containing 75–

78% cobalt, and *black* cobalt(II) dicobalt(III) oxide, containing 70–74% cobalt.

Cobalt(II) oxide, CoO (78.66% Co), is usually prepared by the controlled oxidation of the metal above 900 °C followed by cooling in a protective atmosphere to prevent partial oxidation to Co_3O_4 . Cobalt(II) oxide has a cubic unit cell with $a = 0.425$ nm. It is insoluble in water, ammonium hydroxide, and alcohol, but dissolves in strong acids in the cold and in weak acids on heating. Cobalt oxide (CoO) absorbs a large amount of oxygen at room temperature. Cobalt(II) dicobalt(III) tetroxide, Co_3O_4 (73.44% Co), can be prepared by the controlled oxidation of cobalt metal or CoO or by the thermal decomposition of cobalt(II) salts at temperatures below 900 °C. The cubic spinel lattice has $a = 0.807$ nm; the solid material readily absorbs oxygen at room temperature, but never transforms into cobalt(III) trioxide, Co_2O_3 . The mixed-valence oxide is insoluble in water and only slightly soluble in acids.

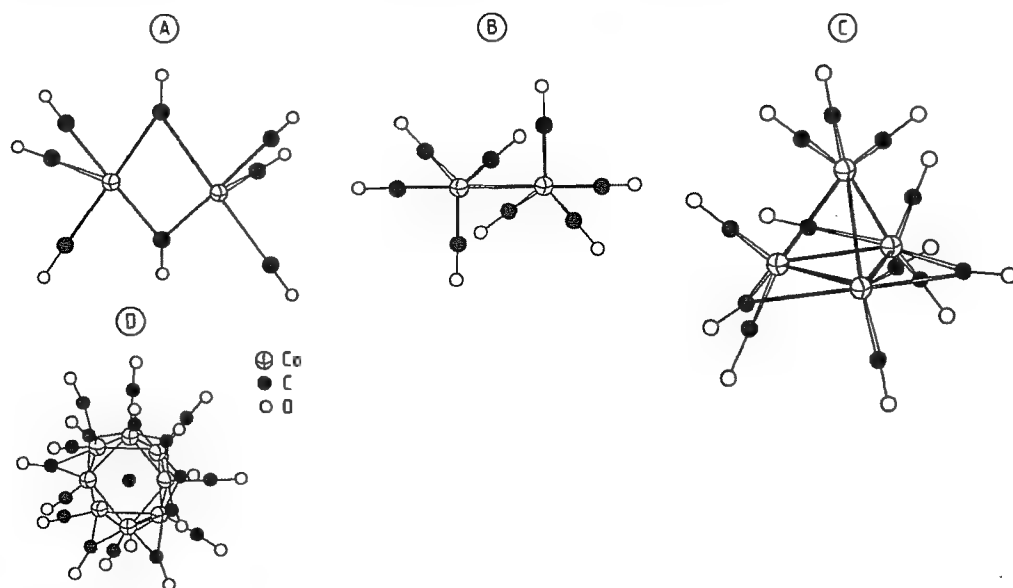


Figure 18.5: Structures of carbonyl complexes of cobalt. A) $[\text{Co}_2(\text{CO})_8]$ (solid state); B) $[\text{Co}_2(\text{CO})_8]$ (solution); C) $[\text{Co}_4(\text{CO})_{12}]$; D) $[\text{Co}_8\text{C}(\text{CO})_{18}]$.

Table 18.11: Industrial uses of cobalt compounds.

Compound	Formula	Uses
Acetate(III)	$\text{Co}(\text{CH}_3\text{COO})_3$	catalyst
Acetate(II)	$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	driers for lacquers and varnishes, sympathetic inks, catalysts, pigment for oil cloth, mineral supplement, anodizing, stabilizer for malt beverages
Acetylacetonate	$\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$	vapor plating of cobalt
Aluminate	CoAl_2O_4	pigment, catalysts, grain refining
Ammonium sulfate	$\text{CoSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	catalysts, plating solutions
Arsenate	$\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	pigment for paint, glass, and porcelain
Bromide(II)	CoBr_2	catalyst, hydrometers
Carbonate	CoCO_3	pigment, ceramics, feed supplements, catalyst
Carbonate (basic)	$2\text{CoCO}_3 \cdot \text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$	chemicals
Carbonyl	$\text{Co}_2(\text{CO})_8$	catalyst
Chloride	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	chemicals, sympathetic inks, hydrometers, plating baths, metal refining, pigment, catalyst
Chromate	CoCrO_4	pigment
Citrate	$\text{Co}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$	therapeutic agents, vitamin preparations
Ferrate	CoFe_2O_4	catalyst, pigment
Fluoride	$\text{CoF}_2, \text{CoF}_3$	fluorinating agents
Fluoride	$\text{CoF}_2 \cdot 4\text{H}_2\text{O}$	catalyst
Fluorosilicate	$\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$	ceramics
Formate	$\text{Co}(\text{CHO})_2 \cdot 2\text{H}_2\text{O}$	catalyst
Hydroxide	$\text{Co}(\text{OH})_2$	paints, chemicals, catalysts, printing inks
Iodide	CoI_2	moisture indicator
Linoleate	$\text{Co}(\text{C}_{18}\text{H}_{31}\text{O}_2)_2$	paint and varnish drier
Manganate	CoMn_2O_4	catalyst, electrocatalyst
Naphthenate	$\text{Co}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$	catalyst, paint and varnish drier
Nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	pigments, chemicals, ceramics, feed supplements, catalyst
2-Ethylhexanoate	$\text{Co}(\text{C}_8\text{H}_{15}\text{O}_2)_2$	paint and varnish drier
Oleate	$\text{Co}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$	paint and varnish drier
Oxalate	CoC_2O_4	catalysts, cobalt powders
Oxide	CoO	chemicals, catalysts, pigments
Oxide	Co_3O_4	enamels, semiconductors
Oxides	(mixed metal)	pigments
Dilanthanum tetroxide	La_2CoO_4	catalyst, anode
Tricobalt tetralanthanum decaoxide	$\text{La}_4\text{Co}_3\text{O}_{10}$	catalyst
Lithium oxide	LiCoO_2	battery electrode
Sodium oxide	NaCoO_2	battery electrode
Dicobalt manganese tetroxide	MnCo_2O_4	catalyst
Dicobalt nickel tetroxide	NiCo_2O_4	catalyst, anode
Lanthanum trioxide	LaCoO_3	oxygen, electrode
Phosphate	$\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	glazes, enamels, pigments, steel pretreatment
Potassium nitrite	$\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot 1.5\text{H}_2\text{O}$	pigment
Resinate	$\text{Co}(\text{C}_{24}\text{H}_{62}\text{O}_4)_2$	paint and varnish drier, catalyst
Succinate	$\text{Co}(\text{C}_4\text{H}_4\text{O}_4) \cdot 4\text{H}_2\text{O}$	therapeutic agents, vitamin preparations
Sulfamate	$\text{Co}(\text{NH}_2\text{SO}_3) \cdot 3\text{H}_2\text{O}$	plating baths
Sulfate	$\text{CoSO}_4 \cdot x\text{H}_2\text{O}$	chemicals, ceramics, pigments
Sulfide	CoS	catalysts
Tungstate	CoWO_4	drier for paints and varnishes

Cobalt(II) Hydroxide. $\text{Co}(\text{OH})_2$ (63.43% Co) is prepared commercially as a pink solid by precipitation from a cobalt(II) salt solution with sodium hydroxide. It has a hexagonal crystal structure with $a = 0.317$ nm and $c/a =$

1.46. It is insoluble in water and alkaline solutions, but dissolves readily in most inorganic and organic acids; for this reason, it is commonly used as a starting material in the synthesis of cobalt chemicals. $\text{Co}(\text{OH})_2$

decomposes thermally by loss of water, starting at 150 °C, to give the anhydrous oxide at 300 °C. Care must be taken to store the hydroxide in the absence of air because slow air oxidation leads to a product that is poorly soluble in weak acids.

Cobalt(II) Chloride. Cobalt(II) chloride hexahydrate, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (24.79% Co), is a dark red deliquescent crystalline compound with a monoclinic unit cell ($a = 0.886 \text{ nm}$, $b = 0.707 \text{ nm}$, $c = 1.312 \text{ nm}$, $\beta = 97^\circ 17'$). It is prepared by concentrating a hydrochloric acid solution of cobalt oxide or carbonate. The chloride is very soluble in water, alcohols, and a number of other organic solvents. The solubility of the chloride in aqueous media does, however decrease with increasing hydrochloric acid content. The hexahydrate dehydrates thermally in three stages, giving the dihydrate at 50 °C, the monohydrate at 90 °C, and the anhydrous chloride at 130–140 °C.

The anhydrous chloride and the lower hydrates are very hygroscopic and transform to the hexahydrate in a moist atmosphere. The fact that the anhydrous chloride is blue and the hexahydrate red is used as a humidity indicator in silica gel desiccants. The chloride is also used in the electroplating, ceramics, glass, chemical, agricultural, and pharmaceutical industries.

Cobalt(II) Sulfate. Cobalt(II) sulfate hexahydrate, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (20.98% Co), is a brownish-red crystalline compound with a monoclinic unit cell ($a = 1.545 \text{ nm}$, $b = 1.308 \text{ nm}$, $c = 2.004 \text{ nm}$, $b = 104^\circ 40'$). It is prepared by concentrating a sulfuric acid solution of cobalt oxide or carbonate. It is an efflorescent substance and loses one molecule of water when exposed to dry air or when heated gently. The hexahydrate obtained loses water in two stages to give the monohydrate at 100 °C and the anhydrous sulfate above 250 °C. The monohydrate, $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ (34.08% Co), has been manufactured and sold commercially. Cobalt sulfates are very soluble in water and are generally more stable than cobalt(II) chlorides or nitrates; for this reason they have been widely used as sources of cobalt(II) in solution

for the manufacture of chemicals and for the electroplating industries. The sulfates are also used in the ceramics, linoleum, and agricultural industries.

Cobalt(II) Nitrate. Cobalt(II) nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (20.26% Co), is a red-brown crystalline compound with a monoclinic unit cell ($a = 1.509 \text{ nm}$, $b = 0.612 \text{ nm}$, $c = 1.269 \text{ nm}$, $\beta = 119^\circ$). It is prepared by concentrating a nitric acid solution of cobalt oxide or carbonate. The hexahydrate loses water rapidly at 55 °C to give the trihydrate; the monohydrate can also be prepared. The nitrates are very soluble in water, alcohols, and acetone. Cobalt nitrate is an important source of high-purity cobalt for use in the electronics and related industries, and the compound has also found uses in the chemical and ceramics industries.

Cobalt(II) Phosphate. Cobalt(II) phosphate octahydrate, $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (34.63% Co), is obtained as a purple flocculent precipitate when an alkali-metal phosphate is added to the solution of a cobalt(II) salt. The phosphate is soluble in inorganic acids and particularly in phosphoric acid, but is insoluble in water or alkaline solutions. It is used in the paints and ceramics industries and is a component of some steel phosphating formulations.

Cobalt(II) Carbonate. Although pure CoCO_3 has a cobalt content of 49.57% and a pseudohexagonal unit cell, the material available commercially is a mauve basic carbonate, $[\text{CoCO}_3]_x \cdot [\text{Co}(\text{OH})_2]_y \cdot z\text{H}_2\text{O}$, of indeterminate composition and a cobalt content of 45–47%. The basic carbonate is insoluble in water, but dissolves easily in most inorganic and organic acids. For this reason it is often used as a starting material for the manufacture of other chemicals. The basic carbonate is also used in the ceramics and agricultural industries.

Cobalt(II) Acetate. Cobalt(II) acetate tetrahydrate, $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (23.68% Co), is a deliquescent mauve-pink crystalline compound with a monoclinic unit cell ($a = 0.847 \text{ nm}$, $b = 1.190 \text{ nm}$, $c = 0.482 \text{ nm}$, $\beta = 94^\circ 18'$). It is prepared by concentrating solutions of co-

balt hydroxide or carbonate in acetic acid. The tetrahydrate is soluble in water, alcohols, inorganic, and organic acids including acetic acid. The compound loses its water of crystallization at ca. 140 °C. It is used in the manufacture of drying agents for inks and varnishes, fabrics, dressings, catalysts, and pigments, as well as in the anodizing and agricultural industries.

Cobalt(II) Oxalate. Cobalt(II) oxalate dihydrate, $\text{Co}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (32.23% Co), is obtained as a pink precipitate when oxalic acid or an alkali-metal oxalate is added to the solution of a cobalt(II) salt. The dihydrate loses water when it is heated gently in air, and at 200 °C it decomposes to cobalt(II) oxide. The oxalate is insoluble in water, slightly soluble in acids, but soluble in solutions containing ammonia or an ammonium salt. The main use of cobalt oxalate is as a starting material for the preparation of cobalt metal powders.

Cobalt(II) Carboxylates. The cobalt salts of carboxylic acids can be made by the direct reaction of cobalt powder, oxide, or hydroxide with the organic acid or by precipitation reactions involving the addition of the sodium salt of the acid to an aqueous solution of a cobalt salt, such as the sulfate. Cobalt(II) resinate, oleate, linoleate, soyate, naphthenate, ethylhexanoate, formate, acetylacetonate, and citrate have been produced for use in a variety of applications including catalysts, drying agents, metal from production, and medical uses.

18.8.3 Industrial Applications of Cobalt Compounds [19]

The more important applications of cobalt chemicals listed in Table 18.12 can be considered under the following headings: glasses, ceramics, and refractories; driers, paints, varnishes, and dressings; catalysts; electroplating; electronics and solid-state devices; and agricultural, nutritional, and medical uses.

Table 18.12: Effects of several elements in cobalt superalloys.

Element	Effect (M = metal)
Chromium	improves oxidation and hot-corrosion resistance; produces strengthening by formation of M_7C_3 and M_{23}C_6 carbides
Molybdenum Tungsten	solid-solution strengtheners; produce strengthening by formation of intermetallic compound Co_3M ; formation of M_6C carbide
Tantalum Niobium	solid-solution strengtheners; produce strengthening by formation of intermetallic compound Co_3M and MC carbide; formation of M_6C carbide
Aluminum	improves oxidation resistance; formation of intermetallic compound CoAl
Titanium	produces strengthening by formation of MC carbide and intermetallic compound Co_3Ti ; with sufficient nickel produces strengthening by formation of intermetallic compound Ni_3Ti
Nickel	stabilizes the face-centered cubic form of matrix; produces strengthening by formation of intermetallic compound Ni_3Ti ; improves forgeability
Boron Zirconium	produce strengthening by effect on grain boundaries and by precipitate formation; zirconium produces strengthening by formation of MC carbide
Carbon	produces strengthening by formation of MC, M_7C_3 , M_{23}C_6 , and possibly M_6C carbides
Yttrium Lanthanum	increase oxidation resistance

18.8.3.1 Glasses, Ceramics, and Refractories

The addition of cobalt oxides to provide a blue pigment for glass, ceramics, and enamels has been used for many centuries. The level of cobalt in the final product depends on the color intensity required, but is typically 0.4–0.5% for colored ceramic bodies, 0.5% for the blue glass used in welder's goggles, and a few mg/kg in camera lens glass. A range of cobalt-containing mixed-metal oxides and cobalt tripotassium hexanitrite (a yellow pigment) is also available for use as pigments. An indication of the colors obtained from mixed-metal oxide pigments is given in Table 18.13. The shades of the colors also depend on the exact composition of the oxide and on the method of preparing the pigment. The compositions of

some ceramic pigments are given in Table 18.14.

Table 18.13: Colors of cobalt-containing pigments.

Metals in mixed-metal oxide	Color
Co Al	blue
Co P	violet
Co Zn	green
Co Sn Si	light blue
Co Cr Al	turquoise
Co Mg	pink
Co Fe	brown

Table 18.14: Compositions of cobalt-containing pigments.

Color	Content of Co ₃ O ₄ , %	Content of other components (% in parentheses)
Mazarine blue	68.0	SiO ₂ (12), cornish stone (16), CaCO ₃ (4)
Willow blue	33.3	CaCO ₃ (50), SiO ₂ (16.7)
Dark blue	44.6	Al ₂ O ₃ (55.4)
Matt blue	20.0	Al ₂ O ₃ (60), ZnO (20)
Blue-green	41.8	Al ₂ O ₃ (39), Cr ₂ O ₃ (19.2)
Black	20.6	Fe ₂ O ₃ (41.1), Cr ₂ O ₃ (32.4), MnO ₂ (5.9)

The pigments are normally prepared by mixing the ingredients as oxides or as readily decomposable salts and then calcining the mixture at 1100–1300 °C prior to milling the product to obtain the pigment as a fine powder. In ceramic applications, the pigments can be added to the ceramic base materials to give a body color or, after being mixed with suitable fluxes, applied as an underglaze (as on Delft china), or overglaze decoration. The final shade after the ceramic has been fired may be modified by reaction between the pigment and the clay base.

Cobalt pigments are used for decolorizing both glass and pottery articles that contain iron oxide, which would give a yellow coloration to the products in the absence of a decolorizer. The yellow color is masked by the complementary blue color of the cobalt pigment added. The levels of cobalt required for the compensation of iron oxide colorations in typical pottery bodies, enamels, and glasses are 0.003–0.02%, 0.002–0.01%, and 1–2 mg/kg, respectively.

The color of the pigments and of the compounds used for decolorizing arise from the

optical absorption spectra of cobalt atoms modified by lattice effects in the pigments and in the final products.

In the vitreous enameling of steel sheet, a small amount of cobalt oxide (0.15–1.0%) is included in the ground coat mixture of feldspar, sand, borax, and soda ash to improve the adhesion of the enamel to the steel. As generally accepted, the cobalt does not contribute directly to the adhesion process, but it is involved in creating suitable conditions for the development of good adhesion.

Ceramic coatings for low-carbon and low-alloy steels for high-temperature use can consist of a mixture of aluminum oxide and two cobalt coats, one of which is high-firing and the other low-firing. The purpose of the latter is to seal off oxygen at low temperatures to protect the base metal from oxidation from the start of the firing. These coatings are claimed to withstand combustion products and corrosive vapors up to 750 °C and have been used to protect flue gas and gas turbine exhaust pipes.

The metal–glass coatings used to protect plain carbon steels typically contain 80% powdered chromium and 20% of a borosilicate glass containing 5% cobalt oxide. Superalloys have also been coated with a ceramic consisting of high-firing cobalt ground coats with high aluminum oxide content or with boron nitride containing a lithium cobalt oxide binding agent.

18.8.3.2 Driers, Paints, Varnishes, and Dressings

A number of cobalt pigments have been used in oil paintings, including Cobalt blue smalt (a silicate), Thenard's blue (an aluminate), Cerulean blue (a stannate), Cobalt violet (a phosphate), and Aureolin yellow (potassium cobalt(III) nitrite). Some of the pigments have also been used for inks, for printing on fabrics and paper, and for coloring plastics.

Cobalt acetate is used for coloring the oxide layers in anodized aluminum to give shades varying from bronze to black. The anodized metal is immersed in a 20% solution of cobalt

acetate and then either in a solution of ammonium sulfide to produce cobalt sulfide (black) or in a solution of potassium permanganate (bronze). The different depths of bronze shades are achieved by different numbers of alternate immersions in the cobalt acetate and permanganate solutions. In addition to its use as a coloring agent, cobalt acetate is also used to improve the lightfastness of anodized aluminum dyed with organic pigments.

The cobalt(II) salts of a number of organic acids have been used as drying agents for non-saturated oils in paints, varnishes, and inks. The salts used for this purpose include the oleate, ethylhexanoate, naphthenate, soyate, linoleate, resinat, and tallate. These cobalt salts are either soluble in the non-saturated oils or they react with them to form soluble compounds that then act both as oxidation accelerators of the oil and as polymerization catalysts, forming a film with increased stability, resistance, and flexibility. The drying action is due entirely to the redox behavior of the cobalt species present, the carboxylate moieties simply act as oleophilic groups to solubilize the cobalt compounds in the oils. The amounts of cobalt added to the oils as drying agents are in the range 0.01–0.6%; the salts can be added as solutions in organic solvents or as dispersions of ultrafine powders. Cobalt-containing drying agents are also used in low-temperature curing processes for silicone resins. The cobalt species promote drying at the surface of the film in contact with atmospheric oxygen. Its action is so fast that a hard polymeric film can be formed that prevents deep drying; for this reason cobalt is often used in conjunction with other metals such as zinc and calcium that do not have a drying action but slow down and control the effects of cobalt.

18.8.3.3 Catalysts [9]

Cobalt compounds are versatile catalysts. Cobalt-containing materials have been used to catalyze the following types of reactions: hydrogenation; dehydrogenation; hydrogenolysis including hydrodenitritification and hydrodesulfurization; hydrotreatment of pe-

troleum products; selective oxidation; ammoxidation; oxidation; hydroformylation; polymerization; selective decomposition; and ammonia synthesis. In addition to these more general reactions, there are a number of reactions for which cobalt chemicals are among the best catalysts. These include their uses as driers, in the oxidation of ammonia to nitric acid, and the syntheses of fluorocarbons.

The effectiveness of cobalt as a catalyst is related to the ease with which the element forms complexes and particularly to the large variety of ligands in these complexes.

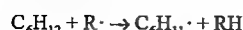
The main industrial processes using cobalt catalysts are the removal of sulfur from various petroleum-based feedstocks (hydrodesulfurization), selective liquid-phase oxidation, and hydroformylation. The catalysts used in the hydropurification reactions including *hydrodesulfurization* consist of cobalt and molybdenum oxides supported on an inert material such as alumina and contain 2.5–3.7% cobalt. The homogeneous catalysts used in the *liquid-phase oxidation* processes are soluble cobalt(II) carboxylates such as acetate, naphthenate, and oleate. Relatively large concentrations of cobalt (0.1–1%) are used as cobalt salts in the catalysis of *hydroformylation* reactions in which HCo(CO)₄ is the active material. The amounts of cobalt catalysts used in hydrodesulfurization, oxidation, and hydroformylation have been estimated at 800–1800, 200, and 800 t/a, respectively.

In *hydrotreating*, the cobalt–molybdenum catalysts function in the sulfide form and catalyze two reactions, hydrogenation and hydrogenolysis of carbon heteroatom bonds. Two theories have been used to explain the enhanced catalytic activity obtained by having both cobalt and molybdenum oxides in the catalysts: the *pseudointercalation model* and the *remote control model*. The first model assumes an association between molybdenum sulfide (MoS₂) and cobalt to produce active sites for the catalysis. The remote control model, on the other hand, assumes that active centers are created in the MoS₂ lattice by a mobile species of hydrogen produced at a cobalt sulfide component. The cobalt in the cata-

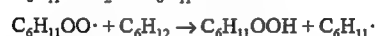
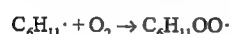
lyst thus controls the nature and the number of catalytically active sites formed.

The types of *oxidations* catalyzed by cobalt salt solutions include *p*-xylene to terephthalic acid, cyclohexane to adipic acid, and hydrocarbons or acetaldehyde to acetic acid. All of these liquid phase oxidations follow classical radical chain mechanisms. The following reaction mechanism for cyclohexane oxidation shows the role of cobalt in decomposing the hydroperoxides formed in the reaction and thus avoiding unwanted side reactions:

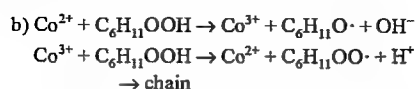
Initiation:



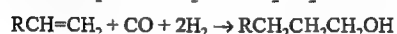
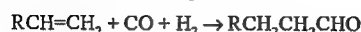
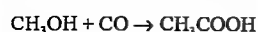
Chain reaction:



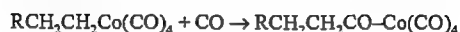
Hydroperoxide decomposition:



In *hydroformylation* and *hydroesterification*, oxo reactions such as those listed below occur:



The cobalt salts added to the reaction mixture are converted into $HCo(CO)_4$, which catalyzes the oxo reaction by the following types of mechanism:



In addition to the main types of reactions catalyzed by cobalt species, cobalt compounds have also been used as catalysts for automobile exhaust gas purification, for the manufacture of nitric acid, for heterogeneous oxidation reactions, and for the oxidation of toluene to

benzoic acid. Cobalt(II) dicobalt(III) tetroxide is one of the most effective catalysts for the oxidation of carbon monoxide and also has a high activity in oxidizing nitrogen monoxide; these properties have led to the use of Co_3O_4 and the $LaCoO_3$ (perovskite phase) as components of exhaust gas purification catalysts. The oxide Co_3O_4 is also a highly selective catalyst in the oxidation of ammonia to nitric acid, although it loses activity due to sintering after repeated use and due to poisoning by sulfur dioxide.

Cobalt is often cited in the patent literature as an additive in nearly all heterogeneous oxidation catalyses, including the oxidations of propene, butane, butenes, and methanol. New systems containing cobalt can also be used to catalyze the conversion of thiols to disulfides in gasoline sweetening.

Cobalt compounds have considerable potential in *homogeneous catalytic systems* and are used with copper in the oxidation of toluene to benzoic acid; good selectivities for the conversion of methanol to ethanol have been achieved by using cobalt cluster catalysts.

Cobalt fluoride can be used as a catalyst in the *fluorination* of hydrocarbons. These reactions utilize the cobalt fluoride as a fluorine carrier and take place in two steps – oxidation of CoF_2 to CoF_3 at 150–200 °C followed by fluorination of the hydrocarbon at 250–350 °C. Both stages of the reaction are exothermic, and careful control of the reaction is needed to obtain optimum yields.

Cobalt has been a component of the catalysts used in the *Fischer-Tropsch synthesis* of hydrocarbons from synthesis gas. The mixed cobalt–thorium oxide–magnesium oxide–kieselguhr catalyst (100:5:8:200), for example, is generally prepared by boiling solutions of sodium carbonate containing cobalt and thorium nitrates to precipitate the metals as carbonates prior to adding magnesium oxide and kieselguhr. The mixture of metal carbonates and support materials is then filtered off, washed, dried, milled, and reduced in a hydrogen atmosphere to produce the Fischer-Tropsch catalyst.

Table 18.15: Compositions of cobalt-containing plating baths.

Electrolyte composition			Content, g/L	Metal deposited
Metal salts	Content, g/L	Additives		
$CoSO_4 \cdot 7H_2O$	332	H_3BO_3	30	Co
$CoCl_2 \cdot 6H_2O$	300	H_3BO_3	30	Co
$CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$	200	H_3BO_3	25	Co
$Co(SO_3NH_2)_2 \cdot 4H_2O$	450	$HCoNH_2$	30 ^a	Co
$Co(BF_4)_2$	116–154	H_3BO_3	15	Co
$NiSO_4 \cdot 7H_2O$	240	H_3BO_3	30	Co–Ni
$NiCl_2 \cdot 6H_2O$	45	$NaHCO_2$	35	
$CoSO_4 \cdot 7H_2O$	3–15			Co–W
$CoSO_4 \cdot 7H_2O$	150	NaCl	28	
$NaWO_3$	15–50	H_3BO_3	40	
		Na heptanoate	100	

^amL/L.

Raney cobalt can be prepared by leaching a finely powdered aluminum–cobalt alloy containing 40–50% cobalt with sodium hydroxide at 15–20 °C, which dissolves the aluminum to leave a very active porous cobalt residue. The properties of Raney cobalt are similar to those of Raney nickel, and the materials can be used to catalyze the same types of reaction.

18.8.3.4 Electroplating [16]

Cobalt is readily electrodeposited from a number of electrolyte solutions. Pure plated layers of cobalt are of little commercial value, but cobalt is an important component of a number of alloy electrodeposits. The electrochemical equivalent of cobalt is $1.099 \text{ g A}^{-1} \text{ h}^{-1}$ and, with cathode efficiencies of 90–100% for most electrolytes, the deposition rates are ca. $1 \text{ g A}^{-1} \text{ h}^{-1}$. Solutions of cobalt sulfate, chloride, sulfamate, or fluoroborate have been used as electrolytes. The compositions of typical plating baths are listed in Table 18.15. To obtain a smooth metal deposit at a cathode efficiency of 90–100% and a current density of 5 A/dm^2 , the bath should have a high cobalt ion concentration (65–100 g/L) and should be operated at a temperature of 25–50 °C and a pH of 4–5.

Additions of cobalt sulfate to nickel plating baths have been used to produce bright nickel plates consisting of nickel–cobalt alloys. The proportion of cobalt in the electrolyte controls the composition of the alloy deposited. Since

the deposition potential of cobalt is less than that of nickel, the cobalt–nickel ratio is higher in the deposit than in the electrolyte. A typical bath composition is given in Table 18.15. If this bath is operated at 55–60 °C, pH 4–4.3, and with a current density of $2.5\text{--}4 \text{ A/dm}^2$, an alloy deposit containing 18% cobalt is produced. The cobalt content of the bath must be maintained by the addition of the cobalt salt when nickel anodes are used. Cobalt sulfamate is used as an alternative to cobalt sulfate in some chloride sulfate nickel plating baths.

Cobalt–tungsten alloys with tungsten contents of up to 10% can be deposited from baths containing cobalt sulfate and sodium tungstate (typical electrolyte composition given in Table 18.15). A temperature of 70–90 °C and a pH of 7–9 are used to obtain smooth crack-free cobalt–tungsten deposits. Cobalt–molybdenum alloys can be obtained under similar conditions when sodium molybdate replaces the sodium tungstate in the electrolyte. A number of other cobalt-containing alloys can be obtained as electrodeposits, including cobalt–iron, cobalt–platinum, cobalt–gold, and cobalt–phosphorus.

Electrodeposited cobalt and cobalt alloys have been used as matrices for composite wear-resistant coatings in systems that codeposit suspended particles of materials such as alumina and silicon carbide with the plating metal.

18.8.3.5 Electronics and Solid-State Devices

There has been recent interest in black cobalt oxide, Co_3O_4 , as a selective coating material for high-temperature solar collectors [20]. The cobalt oxide coatings are superior to the black chrome coatings often used. The function of cobalt oxide as a coating intended to operate up to 1000 °C is to concentrate the solar radiation on the collector surface by a factor of up to 2000 times. For this purpose, a high solar absorbance with low infrared emittance is required. Cobalt oxide coatings can be prepared by plating, pyrolysis of cobalt salts on heated substrates, vacuum deposition, and by use of Co_3O_4 -based paints. Table 18.16 gives absorbance and emittance data for cobalt oxide coated solar panels prepared in a variety of ways on different substrates.

Cobalt(II) oxide has been used in thermistors to improve both the resistivity and the temperature coefficient of the resistivity of the device. A number of mixed-metal cobalt oxides have been used in devices, including NiCoO_4 and La_2CoO_4 as anodic materials in water electrolysis, LiCoO_2 as an electrode in lithium batteries, NaCoO_2 as cathodes in sodium batteries, and CoMoO_4 as a fuel cell electrode. Iron oxides doped with cobalt are used extensively in thin-film coatings for magnetic recording tapes.

18.8.3.6 Agriculture, Nutrition, and Medicine

Cobalt chemicals are used to correct cobalt deficiencies in soils and in animals. Soil treatments usually involve top dressings containing cobalt sulfates, whereas treatment of ruminant animals involves the use of either salt licks containing ca. 0.1% of cobalt as sulfate, or concentrated feeds, or pellets of cobalt oxide bound in an inert material such as china clay.

The medicinal uses of cobalt are dominated by the use of vitamin B_{12} . The vitamin is obtained from the mother liquors of the microbial formation of antibiotics such as

streptomycin, aureomycin, and terramycin after the removal of the antibiotic. Vitamin B_{12} and cobalt treatments are used as remedies in certain types of anemia. Cobalt salts, administered intravenously, have been used as an antidote in cyanide poisoning.

The mechanisms of the agricultural and medicinal uses of cobalt chemicals are discussed in Section 18.10.

Table 18.16: Properties of cobalt oxide coated solar panels.

Coating method	Substrate	Absorbance, %	Emittance, %
Plated	Cu, Ni	93	28
Plated	Ni-plated steel	90	7
Plated/thermal decomposition	Ag-coated steel	> 90	20
Plated	Ni	95	—
Plated	Cu-coated steel	96	13
Oxidized paint	Al	91	30
Paint	Ni alloy	85	10
Spray pyrolysis	Al, galvanized Fe	91, 92	13, 12
Spray pyrolysis	Stainless steel	93	14

18.9 Analysis [21, 22]

Cobalt can be determined gravimetrically as anthranilate, as Co_2O_3 or Co after precipitation of the 1-nitroso-2-naphthol complex and subsequent decomposition, and as a pyridine thiocyanate. Volumetric methods include the use of 8-hydroxyquinoline, ethylenediamine tetraacetic acid (EDTA), and iron(III) cyanide solutions as titrants. In the case of complexometric methods, cobalt is often back-titrated with magnesium or zinc solutions after an excess of EDTA has been added. The metal can also be determined by electrodeposition on perforated platinum electrodes.

Trace levels of cobalt in most materials can be determined by a number of instrumental techniques, including X-ray fluorescence, activation analysis, atomic absorption, atomic emission, and polarography. The reagents that can be used to measure cobalt by colorimetry include dimethylglyoxime, dithizone, 8-hydroxyquinoline, nitrosonaphthols, diethyldithiocarbamate, and tripyridyl.

Table 18.17: Average annual production of refined cobalt in the Western World, t.

Country	Number of producers	1970–1974	1975–1979	1980–1984	1985	
					Production	Capacity
Zaire	1	14 800	12 300	9 250	10 680	17 600
Zambia	1	2 000	2 000	2 850	4 300	5 100
Canada	3	1 900	2 000	3 100	3 710	4 600
Finland	1	900	960	1 400	1 430	1 600
Japan	2	—	1 200	1 900	1 240	2 600
Others	6	1 800	1 700	1 000	520	3 100
Total production		21 400	20 200	19 500	21 880	—
Total utilization		25 500	28 300	31 800	34 600	34 600

Table 18.18: Average annual consumption of cobalt in the Western World, t.

Country	1970–1974	1975–1979	1980–1984	1985
Western World	21 500	19 550	15 900	16 750
North America	8 800	8 400	6 900	7 350
Europe	7 600	6 800	5 400	5 500
Japan	3 700	3 000	2 000	2 400
Others	1 150	1 350	1 400	1 500

18.10 Economic Aspects [23]

Cobalt production and marketing depend very much on the situation in African countries. In May 1978, the economic balance was upset by an invasion of the Shaba province in Zaire by a Katangan army. The result was a drop in cobalt production and a very sharp increase in its price. The dependence of the world's cobalt supply on African producers is shown by the production data in Table 18.17. Western world cobalt production has been increasing at an average rate of 2.8% per year since 1950. Table 18.18 contains the consumption data for cobalt. In addition to primary production, the recovery and recycling of cobalt has become important [24]. During the period 1960–1977, the cobalt price showed a moderate growth pattern of 2.8% in real terms. The 1960 and 1977 average producer prices of the metal were \$3.3 and \$13 per kilogram, respectively. In the period 1978–1979, the price of the metal rose to a maximum of \$108 per kilogram and has since fallen; in early 1985, it was \$24–27 per kilogram.

Cobalt is regarded as a strategic metal in many countries, and a stockpile is held by the

General Services Administration in the United States.

Estimates of cobalt production suggest that in 1990 40 000 t of the metal will be produced in the Western World with a large fraction (68%) still originating in Africa. The outlook for cobalt supplies to the world market is reasonably satisfactory; reserves are large, but the production of cobalt depends on the working of cobalt-containing ores for other metals such as copper and nickel, which will have important economic effects in determining the ores from which cobalt will be produced in the future.

18.11 Physiology and Toxicology [25–29]

The wasting disease in sheep and cattle known as pine in Britain, bush sickness in New Zealand, coast disease in Australia, and salt sick in the United States is treated with vitamin B_{12} . This vitamin is a coenzyme in a number of biochemical processes, the most important of which is the formation of red blood cells.

The acute rat toxicity LD_{50} for cobalt powder is 1500 mg/kg and the TLV is 0.1 mg/m³. Prolonged exposure to the powder may produce allergic sensitization and chronic bronchitis. In 1977 NIOSH recommended that when the cobalt content of cemented carbide dusts exceeds 2%, the dust level should not exceed 0.1 mg/m³ in air. Occupational cobalt poisoning is caused primarily by inhalation of dust containing cobalt particles and by skin contact with cobalt salts. Very few people have been affected by cobalt dust, but those li-

able to be affected must be protected adequately. Skin irritation and diseases caused by cobalt are extremely rare, but it is possible to distinguish two types: one appears as erythema, which is normally found on the hands shortly after contact with cobalt especially during warm weather; the other appears as eczema. However, this form of allergy does not appear until after many years of contact with cobalt compounds.

Toxic effects have been observed from cobalt therapy for certain types of anemia. A single oral dose of up to 500 mg of cobalt chloride has resulted in severe toxic effects, but milder symptoms have been caused by daily intravenous injection of 5–10 mg. In some patients, cobalt has been shown to have a toxic effect on thyroid function.

Over 100 cases of serious heart ailments appeared between 1966 and 1969 in Canada, the United States, and Belgium. They were finally traced to cobalt sulfate that several brewers added to beer (0.075–1 mg/kg) to stabilize the froth. Apparently, chronic alcoholism combined with a lack of nourishment sensitized the hearts of those affected. The acute oral toxicities (LD_{50} , rats) for cobalt oxides, cobalt carbonate, cobalt chloride hexahydrate, cobalt nitrate hexahydrate, and cobalt acetate tetrahydrate are 1750, 630, 766, 691, and 821 mg/kg, respectively [29].

18.12 Pigments

Transparent Cobalt Blue. Cobalt blue, C.I. Pigment Blue 28:77346, is also produced as a transparent pigment by precipitating cobalt and then aluminum as hydroxides or carbonates from salt solutions using alkali. The hydroxides or carbonates are then filtered, washed, dried, and calcined at 1000 °C [30]. It is important to carry out the precipitation with high dilution and to distribute the alkali uniformly throughout the entire reaction volume.

Transparent cobalt blue pigments have the form of small tiles (primary particle size 20–100 nm, thickness ca. 5 nm, specific surface area (BET) ca. 100 m²/g). They are resistant to

light and weather and are used in metallic paint, but are of little importance.

Transparent Cobalt Green. Analogous to cobalt blue, a transparent cobalt green spinel, C.I. Pigment Green 19:77335, can be manufactured.

The green, as well as the blue transparent cobalt pigment, are used as filter materials for cathode ray tubes (CRT) [31].

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Li	Be												B	C	N	O	F	Ne
Na	Mg	Al												Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La [†]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac [‡]																

†	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
---	----	----	----	----	----	----	----	----	----	----	----	----	----	----

‡	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
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19 Beryllium

FRITZ ALDINGER, SIGURD JONSSON, GUNTER PETZOW; OTTO P. PREUSS (§ 19.16)

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19.1 Introduction

Beryllium is the first element in the second main group of the periodic table. It is a light metal with hexagonal-closest-packed (hcp) structure. Both finely divided metal and the compounds have serious toxic effects on the lungs. In addition to the name beryllium, derived from the mineral beryl, this element with atomic number 4 was formerly called glucinium, chiefly in France, because of the pronounced sweetish taste of its salts.

19.2 History

In 1797 VAUQUELIN [1] discovered beryllium oxide while analyzing varieties of beryl including emerald and aquamarine. WÖHLER [2] and BUSSY [3], working independently, prepared elemental beryllium in 1828 by reduction of beryllium chloride with potassium. In 1899 LEBEAU [4] obtained beryllium crystals by electrolysis of molten sodium beryllium fluoride. Industrial production of beryllium began in 1916 in several countries. The publication in 1916 by ØSTERHELD [5] of the phase diagrams of beryllium with iron, nickel, and copper led to the first important use of beryllium in 1931, namely, as an addi-

tive, about 2%, in age-hardenable copper alloys [6].

The demand for beryllium increased around 1950 with the development of nuclear reactors because the nuclear properties and low density of beryllium seemed to indicate that the metal would be especially suitable for nonstationary nuclear reactors of the types used in airplanes, space craft, ships, and submarines [7, 8]. However, beryllium was a disappointment because it swells and becomes brittle when exposed to the simultaneous action of radioactivity and heat [9]. However, the increased research activity in beryllium technology associated with this period produced significant advances in the chemistry, physics, and processing technology of beryllium [7, 10–14].

Since the end of the 1950s, there has been increased interest in beryllium as a structural material, especially in aeronautical and astronautical uses because its mechanical and thermal properties relative to weight are superior to those of all other materials [15–19]. Most of the beryllium produced today is used for military purposes. Greater use in the civilian sector is hindered mainly by the high price, the toxicity, and the room-temperature susceptibility to brittle fracture of the metal. On the

other hand, beryllium oxide is finding increasing use in electrical engineering as an electrical insulator [20]. Beryllium properties, production methods, and applications have been comprehensively reviewed recently [21].

19.3 Physical Properties

The properties listed here were measured, for the most part, on commercial grades of beryllium. These contain various impurities and have various grain structures. Many grades currently available show little similarity to the grades commonly used only a few years ago. The most reliable values of the important physical properties of beryllium [10, p. 320; 18, p. 201; 22–36] are compiled below. On first glance the most outstanding characteristics of the metal are low density and high melting point.

Atomic number	4
Atomic weight	9.0122
Electronic structure	1s ² 2s ²
Atomic radius	112.50 pm
Atomic volume at 298 K	4.877 cm ³ /mol
Crystal structures	
hexagonal closest packed at 293 K	
<i>a</i>	228.56 pm
<i>c</i>	358.22 pm
<i>c/a</i>	1.5677
body-centered cubic at 1523 K	
<i>a</i>	255.0 pm
Melting point	1560 K or 1287 °C
Boiling point	2745 K or 2472 °C
Transformation point	1527 K or 1254 °C
Density at	
298 K	1.8477 g/cm ³
1773 K	1.42
Standard enthalpy	216 J/g
Standard entropy	1.054 J g ⁻¹ K ⁻¹
Heat of fusion	1357 J/g
Entropy of fusion	0.87 J g ⁻¹ K ⁻¹
Heat of transformation	837 J/g
Entropy of transformation	0.186 J g ⁻¹ K ⁻¹
Vapor pressure at	
500 K	5.7 × 10 ⁻²⁹ MPa
1000 K	4.73 × 10 ⁻¹²
1560 K	4.84 × 10 ⁻⁶
Specific heat, at	
298 K	1.830 J g ⁻¹ K ⁻¹
700 K	2.740
Thermal conductivity at 298 K	165 ± 15 W m ⁻¹ K ⁻¹
Linear coefficient of thermal expansion, 298–373 K	11.5 × 10 ⁻⁶ K ⁻¹
Electrical resistivity at 298 K	4.31 × 10 ⁻⁸ Ωm
Magnetic susceptibility at	
93 K	-0.75 × 10 ⁻⁹ m ³ /kg
293 K	-1.00 × 10 ⁻⁹

573 K	-1.20 × 10 ⁻⁹
Hall coefficient	2.4 × 10 ⁻⁹ m ³ A ⁻¹ s ⁻¹
Thermoelectric voltage at 298 K	≈ 5 × 10 ⁻⁶ V/K
Photoelectric work function	3.92 eV
Compressibility	
isothermal	0.0883 × 10 ⁻¹⁰ m ² /N
adiabatic	0.103 × 10 ⁻¹⁰
Speed of sound	12 600 m/s
Surface tension at	
1557 K	1.960 J/m ²
1773 K	1.100
Volume contraction on solidification	3%

The *c*-to-*a* ratio of hexagonal-closest-packed beryllium is very small and decreases with temperature [26]. The existence of the body-centered-cubic high-temperature modification was disputed for many years but has now been demonstrated conclusively [24, 27]. The transformation point is slightly below the melting point [24–28]. The sum of the heats of fusion and transformation is given as 1641 J/g, which allows a heat of transformation of 284 J/g to be estimated [28]. However, a much higher value, 837 J/g, was determined directly [18, p. 201].

The *vapor pressure* values in the literature show considerable variation, probably due to the variable formation of oxide and nitride coatings [37]. They were compiled by HULTGREEN [28]. The high *specific heat* [28] and *thermal conductivity* [7; 10, p. 320; 31] are noteworthy. Low-temperature measurements show that the thermal conductivity perpendicular to the basal plane is greater than that parallel to the basal plane [38].

The coefficient of *linear expansion* is comparatively low. The values given in the literature vary widely, a fact that can be attributed to differences in grain structure of the samples. This is shown by measurements on single crystals parallel and perpendicular to the basal plane [39] and on highly textured material perpendicular and parallel to the pressing direction [40].

The *electrical resistivity* between 40 and 200 K is significantly lower than that of copper or aluminum [41]. Of course, the differences among the reported values are particularly great for electrical properties [11, 22, 31, 36, 42–45] because impurities are especially important here, as has been clearly

shown by measurements of residual resistance in materials of different degrees of purity [46, 47]. The information on the superconductivity of beryllium is contradictory. Some investigators [22, 48] have found *superconductivity* at temperatures below 11 K, others [49] have found superconductivity only in thin films below transition temperatures between 7 and 9 K, and still others [45, 50, 51] have been unable to find superconductivity at all.

Beryllium is *diamagnetic*, little work [33; 34] has been reported on the magnetic properties. The available measurements on the thermoelectric force show considerable variation, probably a result of the experimental conditions and sample characteristics [7, 38, 52].

The reflexivity of beryllium is high, particularly in the infrared region [53]. Beryllium transmits X-rays well because of its low atomic number. Even relatively long-wave gamma rays cause beryllium to emit neutrons, on account of a (γ,n) reaction. Other nuclear reactions of beryllium and its most important nuclear properties [10, pp. 14, 328; 22; 53; 54] are given below and in Table 19.1:

Magnetic dipole moment	5.9468 Am ²
Electric quadrupole moment	0.02 × 10 ⁻²⁴ cm ²
Binding energy of the last neutron	1.664 MeV
Absorption cross section for thermal neutrons (0.025 eV)	
microscopic (σ _a)	0.9 fm ²
macroscopic (Σ _a)	0.0011 cm ⁻¹
Scattering cross section for epithermal neutrons	
microscopic (σ _s)	610 fm ²
macroscopic (Σ _s)	0.76 cm ⁻¹

The nuclear reactions of beryllium with fast neutrons and hard γ rays do not result in long-lived radioactivity. However, additional neutrons and gaseous reaction products may be produced. For example, bombardment with 10²² fast neutrons per cm² generated a total of 23 cm³ of gas per cm³ of beryllium: 5% of this gas was tritium, the remainder was helium [56]. The gas was initially located at interstitial sites or at dislocations. Heating at 1170 K caused the formation of gas-filled pores at the grain boundaries and within the grains, which resulted in a decrease in density of 20%. The volume increase due to pore formation begins at about 870 K. In addition to the formation of noble gases and tritium, normal radiation damage also occurs as a result of elastic colli-

sions of fast neutrons with beryllium atoms [7], but the effect of this radiation damage can hardly be separated from the effect of the gas formation.

The moderator and reflector properties of beryllium for thermal and epithermal neutrons are also favorable [8, 9].

Table 19.1: Properties of beryllium isotopes.

Isotope	Half-life	Radiation, MeV	Source
⁶ Be	0.4 s	—	—
⁷ Be	53.5 d	γ 0.453–0.485	⁶ Li(d,n) ⁷ Li(p,n) ¹⁰ B(p,d) ¹⁰ B(p,α) ¹⁰ B(d,α,n)
⁸ Be	1.4 × 10 ⁻¹⁶ s	α 0.055	⁹ Be(γ,n) ⁹ Be(n,2n)
⁹ Be	stable	—	—
¹⁰ Be	2.7 × 10 ⁶ a	β 0.56–0.65	⁹ Be(α,p) ⁹ Be(d,p) ⁹ Be(n,γ) ¹⁰ Be(n,p) ¹³ C(n,α)
¹¹ Be	—	—	—
Nuclear reactions of the stable isotope ⁹ Be:			
Gamma-ray bombardment		⁹ Be(γ,n) ⁸ Be	
Neutron bombardment		⁹ Be(n,α) ⁶ He ⁹ Be(n,γ) ¹⁰ Be ⁹ Be(n,2n) ⁸ Be	

19.4 Mechanical Properties

As in the case of other metals and alloys, e.g., aluminum or brass, the term beryllium is understood to mean a large group of different beryllium grades, whose properties differ to a greater or lesser extent as a result of differences in recovery and processing. This is also the reason for the more or less large ranges for many properties. Nevertheless, the principles of the deformation modes are known, which is the bridge to an understanding of the mechanical behavior of polycrystalline beryllium.

Beryllium *deforms* primarily on basal planes and secondarily on first-order prismatic planes. Slip systems with a nonbasal Burgers vector, e.g., second-order pyramidal slip, are difficult to activate, especially at room temperature. The strong anisotropy of flow stresses on the active slip systems is illustrated in Figure 19.1. The basal plane has a very low

surface energy and hence acts as a cleavage plane. One main reason for the *brittleness* of beryllium is the fact that the basal plane acts both as the cleavage plane and the slip plane [21, vol. I, pp. 7–114]. Twinning, which is a very important deformation mechanism in several hexagonal closed-packed metals, e.g., zinc, titanium, zirconium, does not play a similar role in beryllium. In beryllium, twinning acts more as a crack inducer or enhances crack propagation, rather than to increase the deformability.

In polycrystalline beryllium brittle fracture occurs even after comparatively low strain at room temperature [11, 15, 57–59].

The reason for this tendency toward brittle fracture is the preferred occurrence of basal slip due to the described strong deformational anisotropy, which induces microcracks [10, p. 372; 60–62]. The brittleness can be reduced by purification of the material (e.g., to reduce oxide content) and special thermomechanical treatment (upset forging), which results in a microstructure with a very small grain size [63].

The average *modulus of elasticity* of beryllium is unusually high, 320 000 MPa, and is strongly anisotropic [64, 65]: 269 000 MPa in the basal plane and 365 000 MPa perpendicular

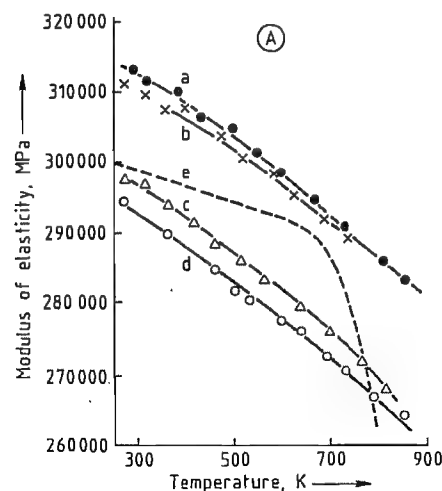


Figure 19.2: Mechanical properties of beryllium as a function of temperature. A) Modulus of elasticity of various grades of beryllium: a) Pressure sintered [66]; b) Cross-rolled cast material [66]; c) Extruded cast material [66]; d) Extruded P/M (powder-metallurgy) material [66]; e) Pressure sintered, 1% BeO [67]. B) Shear modulus and Poisson ratio of cross-rolled cast beryllium [66].

lar to the basal plane [28]. As a result the modulus of elasticity of individual polycrystalline specimens shows considerable variation depending on the type of working, and thus on differences in microstructure (Figure 19.2A). The shear modulus decreases somewhat more rapidly than does the modulus of elasticity as the temperature increases. The Poisson ratio shows a corresponding increase with temperature (Figure 19.2B).

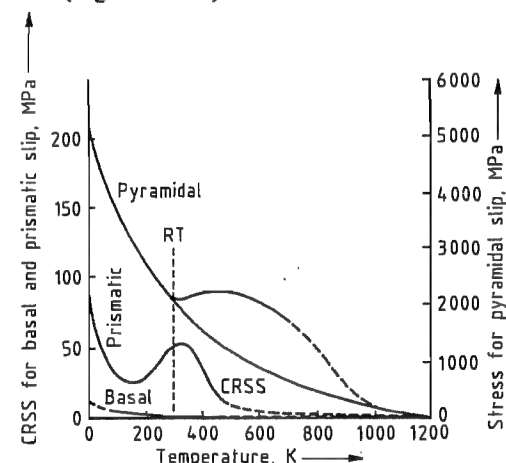
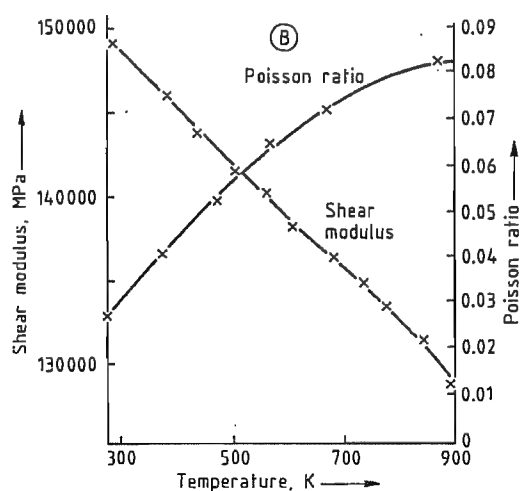


Figure 19.1: Flow stress for basal, prismatic, and pyramidal c + a slip versus temperature [21, vol. I, pp. 7–114]. CRSS stands for critical resolved shear stress.



The deformational anisotropy and susceptibility to brittle fracture become lower as the temperature is increased [10, p. 372] so that beryllium is readily workable above 450 K [57]. However, the *elongation* of some commercial grades of beryllium decreases sharply in the temperature range 650–900 K, then increasing again [15, p. 3; 57; 58] (Figure 19.3, Curves a, b, and c). This decrease in elongation at intermediate temperatures is caused by impurities. However, when the concentrations of aluminum, iron, and beryllium oxide are adjusted in a well-defined manner, the hot-working characteristics can be greatly improved by effective heat treatment [15, p. 112; 68; 69] (Figure 19.3, Curve e). The preferred occurrence of basal slip during warm working, which is usually performed in the temperature range 670–1360 K, also results in a pronounced microstructure. This consists of a preferential orientation of the basal planes, e.g., parallel to the direction of extrusion or parallel to the rolling plane [12, p. 240; 15]. The microstructure strongly limits the basal slip at room temperature in the case of deformation parallel to this preferential direction so that the susceptibility to brittle fracture in this direction of deformation is reduced. Considerable elongation can be attained because of the preferred occurrence of prismatic slip. Perpendicular to the preferred direction of the basal plane the potential elongation is almost equal to zero because the direction of prismatic slip lies in the basal plane.

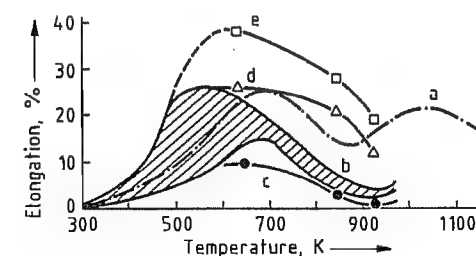


Figure 19.3: Elongation of various beryllium grades as a function of temperature: a) Cast, extruded [57]; b) Pressure sintered [15, p. 3]; c) Pressure sintered, impurities uncontrolled; d) Pressure sintered, Fe and Al content controlled; e) Pressure sintered, BeO, Al, and Fe content controlled [69].

Improvement of the *forming characteristics* by grain refining during melting and casting is possible only to a limited extent [10, p. 136; 12, p. 55; 15, pp. 193, 237, 246; 58; 70–72]. The mechanical properties after powder-metallurgical processing are significantly better than those after casting, and material produced by powder metallurgy is now used almost exclusively.

The susceptibility of beryllium to cleavage fracture is significantly reduced under compressive load so that the deformation values of cast or pressure-sintered material are usually greater than 20%. The buckling strength is comparable to the yield strength; however, the compressive strength is significantly higher than the tensile strength (Table 19.2).

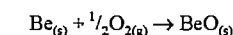
Table 19.2: Strength values, MPa, of extruded beryllium measured in compression test [73].

	Cast		Pressure sintered	
	Room temperature	670 K	Room temperature	670 K
Two-tenths buckling strength	210	179	240	178
Compressive strength	657	460	635	460

19.5 Chemical Properties

The two 2s electrons of beryllium are valence electrons. The first ionization potential ($\text{Be}^0 \rightarrow \text{Be}^+ + e^-$) is 9.32 eV, and the second ($\text{Be}^+ \rightarrow \text{Be}^{2+} + e^-$) is 18.21 eV [74]. Although beryllium is almost always divalent in its compounds, it is far more similar to aluminum than to magnesium or calcium [7, 10, 11, 37, 74, 75]. For example, like aluminum, it is amphoteric, and in humid air and water vapor forms a strongly adhering surface layer of oxide that prevents further oxidation up to about 600 °C [37, 76]. Above 600 °C the oxide layer thickens, but oxidation that destroys the metal by break away does not occur below 700 °C.

The affinity of beryllium for oxygen is very great



$$\Delta G_f^0 (\text{J/g}) = -66469 + 10.5T \pm 4.7$$

and beryllium is an excellent reducing agent. At temperatures $> 900^{\circ}\text{C}$ it reacts violently with nitrogen or ammonia to form beryllium nitride, Be_3N_2 . However, beryllium does not react with hydrogen, even at high temperatures, because the formations of the hydrides BeH_2 and BeH , which are difficult to prepare, are endothermic, and the hydrides rapidly decompose at only slightly elevated temperatures. Below $500\text{--}600^{\circ}\text{C}$ beryllium is not attacked by dry carbon dioxide and is attacked only very slowly by moist carbon dioxide. Beryllium powder reacts with fluorine at room temperature, and at elevated temperatures it reacts with chlorine, bromine, and iodine and with sulfur, selenium, and tellurium vapor; in each case, beryllium burns with a flame.

The adhering oxide film protects beryllium from attack by both cold and hot water. It also protects cold beryllium from attack by oxidizing acids [76]. The stability of the film can be increased by addition of dichromate to the water to form a protective chromate layer as in the case of aluminum. Beryllium dissolves in dilute nonoxidizing mineral acids, accompanied by hydrogen evolution and salt formation. In accord with its amphoteric nature it is also attacked by aqueous hydroxide accompanied by hydrogen evolution and beryllate formation. Since most beryllium compounds have a highly exothermic heat of formation, beryllium reduces the salts and the borates and silicates of many metals. For example, the only halides that are stable towards beryllium are those of the alkali metals and magnesium; all others are reduced by beryllium. Molten alkali-metal hydroxides react explosively with beryllium.

Beryllium forms several intermetallic phases with carbon; all transition metals; the alkaline-earth metals magnesium, calcium, and strontium; and the metalloids boron, arsenic, tellurium, etc. [25]. Some of these phases have extensive homogeneity ranges and high melting points [77–79]. With very few exceptions, the solubility of metals in solid beryllium and vice versa is very low, even at high temperatures. The binary and ter-

nary beryllium systems were reviewed [21, vol. 1, pp. 235–305].

Beryllium is very stable towards liquid lithium, sodium, potassium, zinc, magnesium, cadmium, mercury, gallium, indium, tin, lead, antimony, and bismuth. Some of these metals do not dissolve beryllium at all, even at high temperatures, so long as oxygen is not present. If the melts contain metal oxides, the metal oxides are reduced by beryllium with the formation of beryllium oxide. The layer of BeO formed in this way is not adherent and is removed by the melt, so that a fresh surface of beryllium is always available for reduction.

Beryllium is very reactive in the liquid state, reacting with most oxides, nitrides, sulfides, and carbides, including those of magnesium, calcium, aluminum, titanium, and zirconium.

19.6 Resources, Raw Material

Beryllium is a rare element; its abundance in the earth's crust is about 6 ppm. However, it occurs in concentrated form in various minerals. The total exploitable world reserves of beryllium are estimated at 200 000 tons.

The first beryllium mineral commercially exploited was *beryl*, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, *mp* 1650°C , ρ $2.67\text{--}2.76\text{ g/cm}^3$, hardness of 7.5–8 on the Mohs' scale, optically negative with weak double refraction, $n = 1.57\text{--}1.60$. It crystallizes in hexagonal prisms, which are often very large in size; indeed, crystals weighing several tons have been discovered. It is found in mica schist, granite, pegmatite, and argillite. The crystals often show signs of weathering, and only rarely do they have the ideal composition. Beryl contains about 11% beryllium oxide (4% Be) and is often obtained as a by-product of feldspar quarrying. The largest deposits are found in Brazil, Argentina, India, Mozambique, Madagascar, Uganda, Zimbabwe, South Africa, and the USSR. In addition to the aluminum oxide and silicon dioxide, principal impurities in the ores include alkali

metals, alkaline-earth metals, iron, manganese, and phosphorus.

Until the late 1960s, beryl was the only beryllium mineral having industrial importance. In 1969 Brush Wellmann Inc. began the processing of *bertrandite* ores in Utah. This is presently the most important commercial beryllium mineral. Its formula is $4\text{BeO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, but ores contain only 0.2–0.35% Be [19, p. 21]. Chrysoberyl, $\text{BeO} \cdot \text{Al}_2\text{O}_3$; phenakite, $2\text{BeO} \cdot \text{SiO}_2$; euclase, $\text{BeAlSiO}_4(\text{OH})$; and the precious varieties of beryl, emerald and aquamarine, are highly prized as gemstones. About 40 other beryllium-bearing minerals are known.

19.7 Production

Since the density of beryl is close to that of quartz, concentration by density is not possible. Hand sorting has been the chief means of separation. Flotation is successful only for a few ores [80]. An automatic machine, the Beryl Picker, has been used recently [81]; the ore is first γ -irradiated to render the beryllium atoms radioactive, $^9\text{Be}(\gamma, n)^8\text{Be}$. The beryl crystals are then selected out by a sorter guided by a neutron counter [82].

The recovery of beryllium from both beryl and bertrandite includes several stages. The ores are first converted to an acid-soluble form by fusion. Complex chemical processes are then used to obtain comparatively pure beryllium hydroxide or oxide and then beryllium chloride or fluoride. These halogenides are reduced to metallic beryllium with other metals or by melt electrolysis. The beryllium metal obtained is subjected to one or more refining processes and then to further treatment by powder metallurgy or in some cases fusion metallurgy [7, 10–12].

19.7.1 Processing of Beryl

Beryl is treated mainly by the sulfate and fluoride processes. The chloride process is a direct, inexpensive process for recovering beryllium chloride for electrolysis [10, p. 102].

Other processes are not used because of problems with reactions and apparatus [11, 83].

Sulfate Process. First the beryl, which is only slightly soluble in sulfuric acid even under such extreme conditions as heating for several hours in an autoclave at 400°C , is subjected to either an alkali or a heat treatment.

The *alkali treatment* corresponds to the usual silicate treatment of analytical chemistry: finely ground beryl is heated until fusion or sintered below the melting point with a sufficient quantity of alkaline flux. Suitable alkalis include hydroxides or carbonates of sodium, potassium, and calcium; mixtures of these carbonates; calcium oxide; borax; lead chloride; and sodium sulfate and charcoal. The mechanism of the fusion is still not fully understood [84]. The ratio of flux to beryl depends on the operating conditions, especially the temperature: the higher the temperature the less flux. For alkali treatments involving molten material, gas-heated or oil-heated rotary furnaces or blast furnaces are suitable. Rotary kilns, muffle furnaces, or tunnel kilns are used for sintering.

In the *heat treatment* the beryl is melted (*mp* 1650°C) without additives and then quenched in water. After this treatment about 50–60% of the beryl has a greater solubility in sulfuric acid. The rest of the beryllium oxide forms a solid solution with silicon dioxide that is not attacked by sulfuric acid. At 900°C this solid solution separates into its components, and a heat treatment at this temperature produces a free beryllium oxide that is soluble in sulfuric acid. Such a two-stage heat treatment renders a total of 90–95% of the beryl soluble.

The heat-treated beryl is extracted with hot concentrated sulfuric acid, whereas alkali-treated beryl is extracted with cold sulfuric acid. In the second case there is no heating cost, but the total consumption of acid is greater because of the alkali added. The liquor is diluted with water, and the insoluble silicon dioxide separated by filtration. At this point the filtrate contains not only beryllium and aluminum sulfate but also considerable quantities of iron sulfate and smaller amounts of

other impurities, all of which must be removed before precipitation of beryllium hydroxide. Examples of the many separation methods [11] include the alum separation, the ammonium carbonate separation, and the chelate separation.

In the *alum separation* excess ammonium or potassium sulfate is added to the hot sulfate solution. Upon cooling, all the aluminum precipitates as alum and can be separated from the beryllium sulfate solution in a centrifuge. The filtrate is diluted and then oxidized with potassium permanganate. It is then heated to the boiling point, and calcium carbonate slurry is added until a pH of 3.8–4.2 is reached. This causes iron and manganese to precipitate as the hydroxides and calcium to precipitate as calcium sulfate dihydrate. The beryllium hydroxide is then precipitated by addition of ammonia.

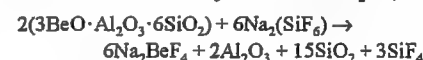
In the *ammonium carbonate separation* the liquor obtained from the fusion treatment is treated with saturated ammonium carbonate solution to precipitate aluminum, iron, and other heavy metals as hydroxides, which are then separated by filtration. The filtrate, which contains the soluble beryllium hydroxide, is concentrated by boiling to precipitate readily filterable sparingly soluble basic beryllium carbonate, which is converted to low-density beryllium oxide by calcining at low temperatures.

In the *chelate separation* iron and aluminum are chelated, e.g., with ethylenediamine-tetraacetic acid. The beryllium can be precipitated as hydroxide, while these complexes remain in solution.

If the separation process does not lead directly to fine-grained, readily filterable beryllium hydroxide or oxide, the fusion liquor is adjusted to pH 7.5 with ammonia or sodium hydroxide and then heated to 95–98 °C. A crystalline, readily filterable beryllium hydroxide is obtained under these conditions. At lower pH gelatinous hydroxide is obtained; at higher pH, amorphous hydroxide is obtained [11]. If the temperature is too low, the crystalline hydroxide forms too slowly.

Brush Wellman Inc., the world's largest beryllium producer, has fully automated its process, called the caustic process. This process uses a heat fusion treatment and is characterized by low consumption of sulfuric acid, reliable separation of iron and other heavy metal impurities by combined alum and chelate separation, and recovery of an easily filterable beryllium hydroxide by hydrolysis of the sodium beryllate [10, p. 71].

Fluoride Process. In the fluoride process beryl is melted or sintered at ≈ 700 °C with sodium hexafluorosilicate. Only the beryllium oxide is converted to a water-soluble salt; aluminum oxide, silicon dioxide, and other impurities are essentially unattacked [83, 85]:



The formation of other beryllium salts (NaBeF_3 , BeF_2) is not observed. Water-soluble Na_3AlF_6 may also be formed in small amounts.

Other suitable extracting agents are hydrogen fluoride at 630 °C, molten fluorides, other fluorosilicates, or silicon tetrafluoride [86]. Rotary kilns are used for reaction with the gases; the solid mixtures are briquetted and sintered in muffle furnaces or tunnel kilns.

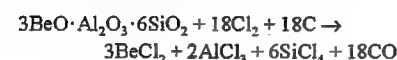
The sodium hexafluorosilicate needed for the fluoride process is relatively expensive. However, consumption can be greatly reduced by adding sodium fluoride [87] or sodium carbonate [88], which traps and thus "recycles" the liberated silicon tetrafluoride.

The sodium fluoride remaining in solution after precipitation of the beryllium hydroxide can also be recovered. Sodium hexafluoroferrate(III) is obtained by precipitation with iron(III) sulfate [89] and can be used instead of sodium hexafluorosilicate.

The reaction product must be leached with water at room temperature because silicon dioxide is attacked by fluoride solutions at elevated temperatures. On the other hand, the leaching must be performed as rapidly as possible because otherwise the beryllium salt that is already dissolved will precipitate [11] and in this form it is sparingly soluble, unlike the

form which is present in the original fusion product. In order to obtain beryllium hydroxide the solution is made alkaline with NaOH. Beryllium hydroxide precipitates when the solution is diluted with water and then boiled. The fluoride process is being tested in a pilot plant by Bhabha Atomic Research Centre, India [90].

Chloride Process. At temperatures above 630 °C the components of beryl can be extracted in a stream of chlorine; reducing conditions greatly enhance the yield:



In practice a mixture of pulverized beryl and carbon is either heated near 800 °C in a stream of chlorine [91, 92] or melted in an electric-arc furnace. In the second case the carbides that form are chlorinated [93, 94]. The reaction can also be carried out with gases that contain chlorine, such as hydrogen chloride [83], carbon tetrachloride [95], sulfur chloride [83], or phosgene [96, 97]. The volatile chlorides are separated by fractional condensation or liquid–liquid extraction with sulfur dichloride, sulfuryl chloride, phosphorus trichloride, phosphorus oxychloride, boron chloride, carbon tetrachloride, or phosgene [83].

Reducing chlorination of the beryllium hydroxide or oxide obtained in the sulfate or fluoride process gives beryllium chloride, the starting material for the electrolytic production of beryllium.

19.7.2 Processing of Bertrandite

The beryllium-poor bertrandite ores (≤ 0.5 – 0.8% BeO) discovered in the United States in 1960 cannot be economically smelted by conventional methods. A new process was therefore developed by Brush Wellman Inc., called the *SX-Carbonate process* (Figure 19.4) [98, 99]. This process produces a very pure beryllium hydroxide (Table 19.3) by liquid–liquid extraction with organic phases [74].

Table 19.3: Typical analyses of beryllium hydroxide obtained by two processes, ppm, with respect to BeO [98, 99].

Element	SX-Carbonate process	Caustic process
Al	200	3000
Fe	200	1300
Cr	50	125
Li	70	300
Mg	100	6000
Mn	10	900
Ni	10	30
Na	500	10000
Ca	200	800
Cu	5	25
Si	100	1500
Zn	20	700

Unlike beryl, bertrandite is soluble in sulfuric acid without pretreatment. The insoluble residue (SiO_2 , etc.) and the aluminum content, which precipitates as an aluminum alum, are removed. The sulfate solution, pH = 0.5, then contains the beryllium and also aluminum, calcium, iron, sodium, and traces of other elements.

The sulfate solution is extracted with a 0.3 M solution of ammonium di-2-ethylhexyl phosphate/di-2-ethylhexyl phosphoric acid/kerosene (DAP) in a five-stage mixer at ≈ 50 °C. In the first mixer the pH is about 2, and after the last stage it is about 5.5. The acid strength is adjusted in a well-defined manner in each stage by means of the ratio of the ammoniacal to the acid component of the organic phase. Beryllium, aluminum, and iron enter the organic phase almost quantitatively, while the other impurities remain in the sulfate solution. Following separation of the two liquid phases, the metal ions are removed from the organic compounds by a 3.0–3.5 m ammonium carbonate solution in a two-stage mixer. This results in the formation of a basic beryllium carbonate solution, which is actually a slurry since it contains precipitated aluminum hydroxide (the ABC slurry). The organic phase, which is now free of metal ions, is returned to the process after purification. Iron is precipitated from the ABC slurry by heat treatment, 45 min at 85 °C, and filtered off with the aluminum hydroxide. The beryllium remains in solution as basic carbonate.

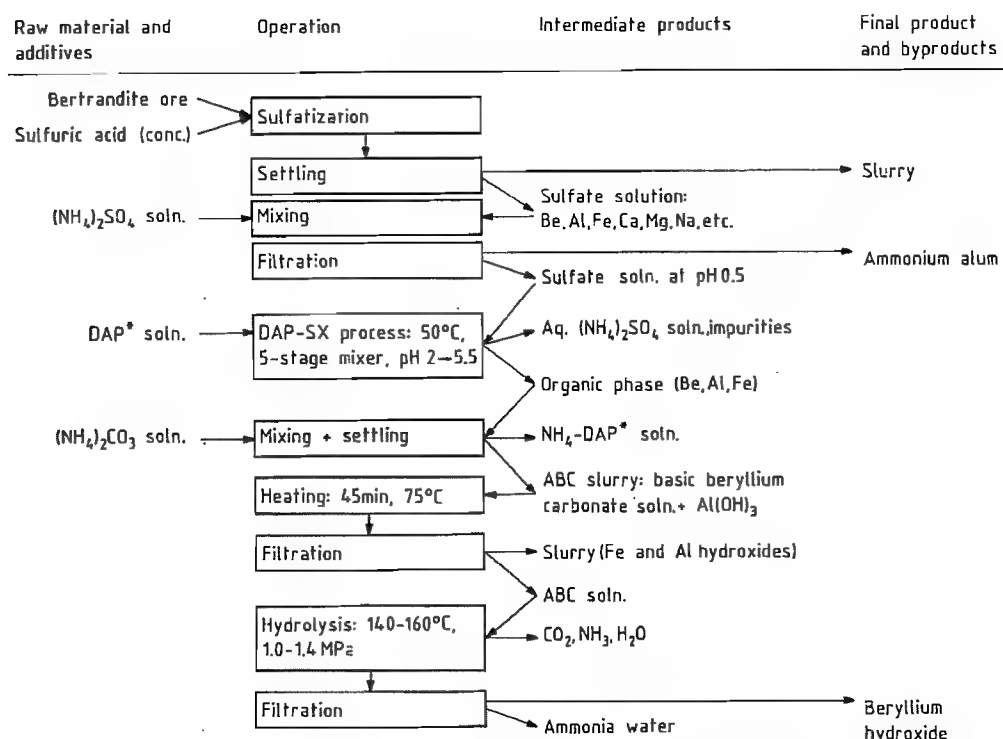


Figure 19.4: Flow diagram of the SX-Carbonate process (Brush Wellman Inc., USA) [98-99]. DAP is the abbreviation for the solution ammonium di-2-ethylhexyl phosphate-di-(2-ethylhexyl) phosphoric acid-kerosene.

The specified time must be observed as closely as possible: if the heat treatment is too short, iron is only partially precipitated. If it is too long, the beryllium loss will be too great. Even so, about 2% of the beryllium is coprecipitated and about 4-6% is contained in the hydroxide filter cake. Half of the beryllium can be separated by careful washing. The remainder is recovered by dissolving the precipitate in sulfuric acid, extracting the iron with an organic phase, and recycling the beryllium- and aluminum-containing sulfate solution to the process before the alum precipitation.

The basic beryllium carbonate solution separated from the ABC slurry by filtration is decomposed in an autoclave (140-160 °C, 1.0-1.4 MPa) into ammonia, carbon dioxide, and a beryllium hydroxide that is easily filtered off and that is quite pure (Table 19.3). The ammonia and carbon dioxide are used to produce ammonium carbonate, which is returned to the

process. The ABC slurry can be treated additionally to further reduce the concentration of impurities, e.g., to reduce the iron content to less than 50 ppm. For this reason beryl ores are today also treated by the SX-Carbonate process, following the usual heat treatment.

19.7.3 Production of Reducible Compounds

The most important metal production processes are based on reduction of beryllium fluoride by magnesium and beryllium chloride by melt electrolysis. Therefore, the beryllium hydroxide or oxide obtained from the fusion process must be converted into one of these halides.

Beryllium Fluoride. First beryllium hydroxide is dissolved in an ammonium hydrogen fluoride solution. The resulting ammonium tetrafluoroberyllate is dissociated to such a

small extent in the solution that the pH can be varied over a wide range without beryllium hydroxide precipitating. Impurities can thus be precipitated relatively easily as hydroxides. Aluminum is precipitated as hydroxide by increasing the pH to 8.3. Chromium and manganese are precipitated by oxidation with lead dioxide, and manganese is precipitated by oxidation with lead dioxide and manganese dioxide. Copper, nickel, and lead are precipitated as sulfides.

Ammonium tetrafluoroberyllate is freely soluble in water. When concentrated by evaporation, it crystallizes without water of hydration. Above 130 °C it dissociates into ammonium fluoride and beryllium fluoride. Between 900 and 1100 °C ammonium tetrafluoroberyllate dissociates into gaseous beryllium fluoride and gaseous ammonium fluoride. The latter can be recycled to the process as ammonium hydrogen fluoride by dissolution in aqueous hydrogen fluoride. Cooling produces beryllium fluoride as vitreous grains [10, p. 71; 100].

Beryllium Chloride. Beryllium chloride can be prepared either directly from beryl by the chloride process or by chlorination of beryllium oxide under reducing conditions [101].

Beryllium chloride is especially well suited for purification by distillation in a stream of hydrogen [10, p. 102] and fractional condensation [102]. The significantly lower-boiling chlorides of aluminum, silicon, and iron(III) can be separated by careful temperature control. Iron(II) chloride, which is reduced by hydrogen, stays in the residue.

19.7.4 Metal Production

The chief difficulties involved in the production of beryllium metal are the reactivity and high melting point of the metal and the extreme stability of the oxide. Of the many possible methods of producing beryllium [10, 11, 84] two are used in industry presently: fusion electrolysis and reduction of halides by metals.

Only calcium is able to reduce the extremely stable beryllium oxide directly under

standard conditions. However, calcium forms the very stable intermetallic compound CaBe [103]. Reduction of BeO with titanium, zirconium [104], or carbon [105] at high temperatures is theoretically possible: the volatile beryllium would have to be distilled off from the reaction zone immediately. However, this method is not used.

Reduction with Metals. The most important industrial process is the reduction of beryllium fluoride with magnesium [10, p. 71; 106-109], the process presently used by Brush Wellman Inc.

The reaction is started by heating a mixture of relatively coarse-grained beryllium fluoride and magnesium in a graphite crucible. At a temperature of about 1300 °C the reaction produces a mixture of beryllium pebbles and magnesium fluoride. The reaction cannot be performed without external heating because the heat of reaction is not great and because the beryllium fluoride must be processed in the form of relatively large particles due to its toxicity and hygroscopicity. Normally about 70% of the stoichiometric quantity of magnesium is used. In this way a readily water-soluble beryllium magnesium fluoride slag, easily separated from the coarse-grained beryllium, is produced. The unreacted beryllium fluoride is separated from the magnesium fluoride and returned to the process.

The reaction of beryllium chloride with magnesium or sodium or the reaction of beryllium fluoride with sodium cannot be carried out in the same way. Sodium is more difficult to work with because of its low boiling point and its reaction with graphite. Beryllium chloride (*bp* 520 °C) is too volatile. The reduction of beryllium chloride with sodium in the vapor phase at 250 °C is the only process developed to the production stage [110-112]. However, this process does not currently have any economic importance.

Fusion Electrolysis. All practical electrolytic methods of production are based on the decomposition of beryllium fluoride, beryllium oxide, or beryllium chloride mixed with halides of the alkali metals or alkaline-earth met-

als [83]. These main group I and II halides are necessary to form a stable melt electrolyte with good conducting properties — the molten beryllium halides are covalently bonded and thus poor electrical conductors. In addition, only beryllium fluoride has a sufficiently large interval between melting point and boiling point at atmospheric pressure.

The electrolysis of the fluoride was developed by A. STOCK, H. GOLDSCHMIDT [113], Siemens & Halske [114], and the Beryllium Research Society. The electrolysis was carried out above the melting point of beryllium, at 1290–1400 °C. These methods and the similar methods of J. DICKINSON [115] and A. C. VIVIAN [116] are now obsolete.

The electrolysis of beryllium chloride [117] can be carried out at temperatures so low that the metal neither melts nor oxidizes. The beryllium is obtained as solid flakes, which are separated by washing out the electrolyte.

Mixtures of approximately equal parts of beryllium chloride and sodium chloride are electrolyzed at ≈ 350 –400 °C. The composition of the electrolyte is held as constant as possible. The apparatus consists of two identical nickel vessels hanging in electric furnaces. The crucible covers are fitted with the connections. One of the covers contains the anode and can be placed alternately on each crucible, the crucibles themselves serve as cathodes. During electrolysis (4–6 V, 0.08 A per cm² of cathode surface area) the metal is deposited as flakes on the cathode wall. When the beryllium chloride concentration in the melt has fallen to 45%, the melt is siphoned into the second crucible, in which beryllium chloride and sodium chloride have previously been melted down in quantities corresponding to the quantities consumed by the electrolysis in the first crucible. In this way the bath is again given its original composition. The crucible covers are then exchanged, and electrolysis is started in the second crucible. The chlorine generated at the anode during electrolysis is collected and used in the production of beryllium chloride.

The equipment for this process was developed by Degussa. Since the Second World

War this process has been used by Pechiney Cie. Chloride electrolysis was also used in France by Tréfinmétaux G.P., a joint subsidiary of Pechiney Cie. and Kawecki Berylco Ind. Inc., and by NGK Insulators in Japan. It was used in slightly modified form by Murex Ltd., England [10]. It is also used in the former Soviet Union [118].

19.7.5 Refining and Further Processing

The as-reduced beryllium pebbles or flakes still contain many impurities and have to be refined before they are used to fabricate structural pieces. The main impurities in electrolytic beryllium are sodium and chlorine. The main impurities in beryllium from the magnesium reduction process are magnesium and magnesium fluoride. Other impurities include beryllium oxide, carbon, and metals, the most important being aluminum, iron, and silicon. Typical analyses of magnesium-reduced beryllium and electrolytic beryllium (CR flakes, Pechiney Cie.) are given in Table 19.4. Some of the impurities have adverse effects on the mechanical properties and corrosion of beryllium or are reactor poisons. Commercial grades of beryllium are refined exclusively by vacuum melting in beryllium oxide or magnesium oxide crucibles and casting in graphite ingot molds. The ingots weigh ≈ 200 kg. Their surfaces are machined (skinned) to remove the high carbon content material adjacent to the mold wall.

The melting of magnesium-reduced beryllium in a high vacuum produces a degree of purity comparable to that of electrolytic beryllium. Melting the electrolytic flakes in a vacuum further reduces the content of halides and low-boiling metals. A very pure grade of beryllium, particularly with respect to the content of oxide, aluminum, iron, silicon, carbon, and halides, can be produced by electrolytic purification (SR flakes, Pechiney Cie.). Other methods, such as vacuum distillation [10, 11, 18, 119–123], zone melting [18, 47, 124, 125], or liquid-metal extraction [18] have been used in the laboratory only.

Table 19.4: Composition of beryllium produced by various methods, ppm [12].

Element	Mg-reduced, coarse-grained	Electrolysis	
		CR flakes	SR flakes
O	—	2300	500–800
Al	400	< 200	60
Fe	500	300	50
Ni	100	150	30
Si	50	75	30
B	—	2	2
Cr	100	20	5
Mn	100	60	30
Ca	—	200	30
Mg	15 000	50	30
Na	—	300	—
C	300	300	150
F	20 000	—	—
Cl	—	1000	700
Be, %	96.0	96.5	99.87

Melting and Casting. The main purpose of melting and casting of beryllium is purification (see above); the production of semifinished goods is of secondary importance [12, p. 55]. The reason for this is that parts produced from castings have significantly poorer properties, even after working, than parts made by powder metallurgy. Cast flaws due to gas evolution during solidification and transcrystalline microcracks [10, p. 136; 15, p. 677] caused by cooling stresses cannot be prevented, even though they can be greatly reduced by mold design and construction [126]. Another significant disadvantage is the coarse-grained texture that develops during solidification, resulting in poor mechanical properties not improvable by thermomechanical treatment [10, p. 136; 12, p. 55; 15, pp. 193, 237, 246; 71, 72]. Fairly often crystals several centimeters in length are observed after induction melting [12, p. 55], and often crystals several millimeters in length are observed after electric-arc melting [15, pp. 677, 687; 126]. No effective grain-reducing agent is known [126].

Powder Manufacture. Beryllium was first worked by powder metallurgy in 1946. Since then many methods of powder production and compaction capable of producing ductile beryllium parts with good high-temperature strength have been studied and tested [12; 21,

vol. 2, pp. 13–29; 127]. However, the concentration of impurities is increased during powder-metallurgical working. Atmospheric oxygen and nitrogen, as well as iron and carbon from the mechanical working of the material into powders, are especially important. Above all, there is an increase in the oxide content as the grain size is decreased, i.e., as the specific surface increases. On the other hand, the oxide is desirable in certain circumstances because it increases strength and inhibits grain growth.

Powder manufacturing starts with cast ingots of inherently coarse grain size characterized by low ductility and resistance to fracture. These ingots are chipped with a lathe. The equipment is heavy duty: a multipoint tool can chip a 65-kg ingot in a single pass. These relatively coarse chips must be ground, or otherwise comminuted to finer particle sizes.

The first milling method commercially employed was *rotary grinding* between one stationary water-cooled and one rotating beryllium disk. The coarse chips were fed through a central hole in the stationary disk, and the fine powder emerged peripherally. The mill was enclosed into a sealed system to minimize contamination of the powder and to protect the environment from the toxic beryllium dust. This method was the standard for many years. Almost everywhere it has now been replaced by the impact attrition mill.

Within the *impact attrition mill* the coarse powder is fed into a gas stream, accelerated through a nozzle and impacted against a beryllium target. The morphology of the powder particles comminuted by this process is more spherical and less flat than disk-milled powder. Therefore, the mechanical properties of impact-ground powder compacts are more uniform. Because of the improved isotropy and a lower amount of inclusions and impurities the elongations of beryllium grades produced from impact-attrition material are higher.

Another commercial production process is *ball-milling*. It is used for high-oxide ultrafine powder ($\approx 5 \mu\text{m}$), which is made especially for instrumentation uses. The high microyield

strength specified for such qualities is provided by the fine particle size and the high oxide content that strengthen the grain boundaries within the unpacked material. Because ball-milled powders are flat, like the particles produced by rotary grinding, they are difficult to handle and cause anisotropic physical and mechanical properties in the compacted beryllium billets.

Other powder production methods, like fluid-energy milling, disintegration of beryllium melts by gas atomization, rotating electrode process, or centrifuged shot-casting, have been used only in the laboratory [21, vol. 2, pp. 13–29]. Nevertheless, some of these processes may be used to produce commercial beryllium powder within the foreseeable future.

Powder Consolidation. *Vacuum hot pressing* of beryllium powder in graphite or steel dies is by far the most important commercial consolidation process. The powder is either dynamically compacted in the die or prepressed under cold isostatic conditions. After the die has been heated to 1000–1200 °C, a pressure of 1.4–10 MPa is applied. In this way billets up to 1.80 m in diameter and 6 t in weight, with relative density of nearly 100%, have been manufactured.

Hot isostatic pressing is used to produce more complicated parts with improved isotropic properties. The powders are either directly consolidated in a one-step process or preconsolidated. In preconsolidation the powder is prepressed at 210–700 MPa under cold isostatic conditions in rubber containers, the cold compact degassed at 650 °C, and the compact pressed isostatically for 2–3 h at 70 MPa and 760 °C in evacuated stainless steel containers [128].

The combination of *cold pressing and sintering* has been applied in the production of special parts, e.g., aircraft brake segments. Preforms may be sintered using mandrels to limit distortion and give better shape control. Sintering is usually carried out in a vacuum, which ensures better consolidation and higher densities than those achieved in argon.

The hot-pressed ingots are worked into semifinished goods or finished parts by machining, rolling (760–870 °C), extrusion (900–1090 °C), drawing (400–430 °C), deep-drawing (710–760 °C), forging, and compression (400–430 °C) [13, 14].

During hot deformation the beryllium is usually enclosed in a steel container. Working with such “canned” material greatly simplifies the operation because the workpieces need not be in a vacuum and need to be heated only slightly or not at all. The steel cover reduces oxidation and surface damage, improves lubrication, and produces a uniform temperature distribution in the workpiece. Although hot-deformed parts are usually less expensive than machined parts, they have highly anisotropic properties, with the favorable values in the direction of material flow during deformation and the less favorable values perpendicular to this direction. Cross-rolling produces uniform properties, e.g., in the sheet plane. Other processes used only in special cases are slip casting [21, vol. 2, pp. 13–29; 127; 129; 130], spark sintering [131], sinter forging [12, p. 102; 132], plasma injection [133], and isostatic hot-pressing [128].

Production of Single Crystals. The first comprehensive work on beryllium single crystals was done in the early 1950s [10, p. 372; 134–137]. These crystals were used mainly for investigations of the mechanical and cleavage fracture behavior of beryllium and were produced only in the laboratory. They were grown by slow solidification from the melt in a crucible [10, p. 372; 137], direct crystallization from vapor [138], and crucibleless zone melting [134, 139–145]. Efforts to produce beryllium single crystals using the Bridgman method were unsuccessful [146].

During the late 1970s it was recognized that beryllium would be the most efficient material for neutron monochromators, both because of its excellent nuclear properties and its excellent crystallographic properties [147, 148]. Many attempts to obtain beryllium single crystals with monochromator qualities failed [146, 149–152], but recent improvements in

equipment and technique have opened a new field that will likely lead to single-crystal manufacturing on an industrial scale.

Crystals with a diameter of 15 mm having a proper substructure can be grown by crucibleless zone melting at a rate of 1 mm/min. The application of the necking technique is inevitable. A modified double-ellipsoid mirror furnace, originally developed for crystal growth experiments during spacelab missions, is used [153]. The mosaic spread of the as-grown beryllium crystals can be increased from a few minutes to any desired value by plastic deformation on prismatic planes [154].

19.8 Environmental Protection

Because of the toxicity of beryllium vapor and dust, all operations should be carried out in properly ventilated rooms, and with vented equipment. Source exhaust has been found to be most effective [155–157]. In the presence of poorly controlled high workplace concentrations, fine-dust masks with filters of the specific safety level must be worn. The following limits have been recommended by the U.S. Atomic Energy Commission and the American Conference of Governmental Industrial Hygienists as a guideline for controlling beryllium hazards:

- In-plant atmospheric concentration should not exceed 2 µg/m³ throughout an 8-h working day.
- A brief exposure should not exceed 25 µg/m³.
- In the neighborhood of a plant handling beryllium the average monthly concentration should not exceed 0.01 µg/m³.

In order to meet these safety regulations the plant exhaust air has to be efficiently filtered before it is discharged into the atmosphere. All persons employed in processing areas with high risk potential for beryllium dust exposure are advised to wear shop-laundered work clothes to prevent neighborhood contamination. Care must also be exercised in disposal

of wastes from beryllium facilities: securely packed solid wastes are disposed by ground burial in concrete trenches. Liquid wastes are chemically treated to remove the toxic substances and to bring down the beryllium concentration to a safe level of approximately 1 ppm before discharge into public sewers.

In order to monitor the workplace concentration of 2 µg/m³, dust collectors must have suction speeds between 0.02 and 2 m³/min, depending on the type of sampling [155]. Presently a sufficiently sensitive analytical method for detecting the comparatively low beryllium concentrations is spectral analysis. Metallic beryllium in powder form can burn when ignited by sparks or an external heat source but does not self-ignite or explode. Beryllium oxide and alloys are not combustible. The naturally occurring isotope ⁹Be is not radioactive.

19.9 Quality Specifications

To date there is only one company — Brush Wellman Inc. — in the Western world that produces beryllium, beryllium-rich alloys, and beryllium compounds commercially. Brush Wellman Inc. produces beryllium from bertrandite by the SX-Carbonate process, reduces beryllium fluoride with magnesium, and refines it by vacuum melting and casting. Different grades are produced by different powder-metallurgy processes and metallurgical treatments, e.g., forging, extruding, rolling, and annealing. A high-purity grade, as obtained by electrolytic refining, is not available currently.

The composition, yield strength $\sigma_{0.2}$, tensile strength σ_p , and failure strain δ of several typical, commercial types of beryllium are compiled in Tables 19.5 and 19.6. However, these values guaranteed by the manufacturers are generally exceeded. The vacuum hot-pressed materials of Table 19.5 are used in nuclear technology, aeronautics, astronautics, and wherever high strength is required. The table shows that the yield strength and tensile strength increase with oxide content, while the elongation is not significantly affected. The

brake grade (BG-170) is characterized by greatly reduced hot brittleness (Curve c in Figure 19.3) [68, 69]. In the case of the instrument grades 1-220A and 1-400, the concentration of impurities is used to give a high precision elastic limit (PEL), below which the plastic strain is smaller than 10^{-6} or one microstrain.

The development of texture in extruded parts and plates results in failure strain values of 5 and 10% in the direction of extrusion and in the rolling plane, respectively (Table 19.6); perpendicular to this direction the failure strain is < 1%. Forged parts have elongations of 3%, and high-strength wire ($\phi < 0.25$ mm) has an elongation of 1%.

As an example of the effect of temperature on tensile strength, yield strength, elongation, and necking at failure, the values measured for plate material parallel to the plane of the plate are plotted in Figure 19.5. The plate material was produced by cross-rolling high-purity isostatically hot-pressed ingot material.

The creep rupture strength is usually high [67, 161, 162]. In the case of cross-rolled plates the ten-hour creep rupture strength is equal to the tensile strength up to 800 K and can be significantly increased by carbon or beryllium oxide [37]. The little information that is available on the fatigue strength [161–165] (Figure 19.6) indicates that beryllium has high fatigue strength and that the dynamic crack propagation is much less critical under alternating stress than under normal stress.

Table 19.5: Manufacturer-guaranteed composition and mechanical properties of various grades of beryllium [158].

	S-65B	S-100E	S-200E	I-70A	I-220A	I-400	BG-170
Chemical composition							
Be, min. %	99.0	98.5	98.0	99.0	98.0	94.0	98.0
BeO, max. %	1.0	1.2	2.0	0.7	2.2	4.2 ^a	1.2
Al, max. ppm	600	1400	1600	700	1000	1600	500
C, max. ppm	1000	1500	1500	700	1500	2500	1500
Fe, max. ppm	800	1500	1800	1000	1500	2500	1500
Mg, max. ppm	600	800	800	700	800	800	800
Si, max. ppm	600	800	800	700	800	800	500
Others, each, max. ppm	400	400	400	400	400	1000	—
Tensile properties							
σ_p , min. MPa	290	241	276	241	310	344	345
$\sigma_{0.2}$, min. MPa (0.2% offset)	207	186	207	172	241	—	207
Elongation, min. %	3	1	1	2	2	—	1
Microyield, min. MPa	—	—	—	—	34	55	—

^aBeO specified is minimum in this instance.

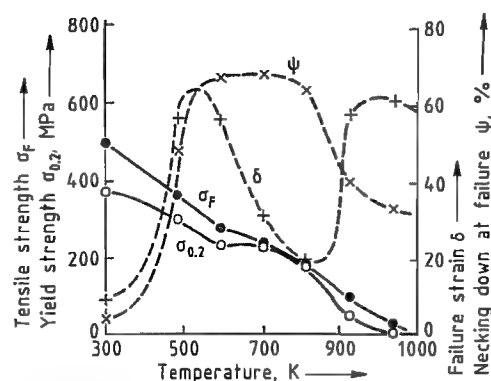


Figure 19.5: Mechanical properties of high-purity beryllium [160].

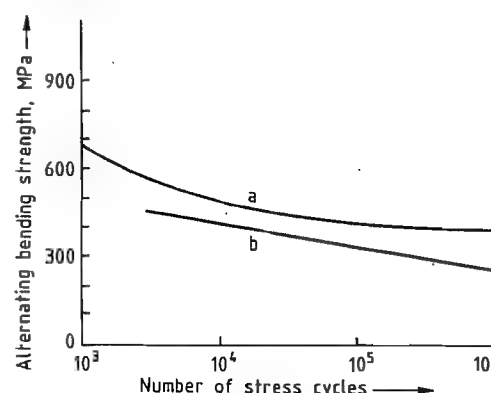


Figure 19.6: Fatigue strength of pressure-sintered, hot-worked beryllium [161]: a) Extruded and forged; b) Cross rolled.

Table 19.6: Mechanical properties of various semifinished beryllium products [158, 159].

	Plates ^a	Extruded parts ^a	Forged parts ^a	Wire, $\phi < 0.25$ mm
BeO content, % max.	2.0	2.0	2.0	0.02
$\sigma_{0.2}$, MPa	350	280	280	760
σ_p , MPa	480	480	450	900
δ , %	10	5	3	1

^aProperties parallel to the direction of extrusion or to the rolling plane.

A compilation [163, 164] of the K_{Ic} (a measure of the toughness) values published so far shows that there is a great deal of variation. Most values lie between 10 and 20 MPa/m^{1/2}, but values up to 40 MPa/m^{1/2} have been reported. However, the impact strength of notched and unnotched specimens is very low and depends on the type of working (Table 19.7).

Table 19.7: Impact strength (Charpy test), 10^{-2} MPa, of beryllium produced in various ways [58].

	Unnotched	Notched
Cast and extruded	0.16	—
Pressure sintered	1.1–3.4	0.68–1.3
Pressure sintered and extruded	5.6–6.1	—
Pressure sintered and rolled	2.7–4.1	—

The hardness of high-purity beryllium (Pechiney SR) is plotted in Figure 19.7 as a function of the mean grain size. The Brinell hardness of commercial pressure-sintered beryllium varies between 100 and 200, depending on the composition of the tested material [52].

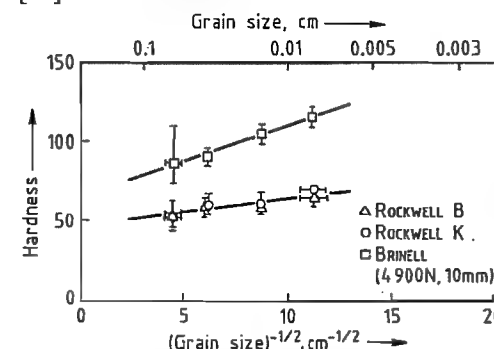


Figure 19.7: Brinell and Rockwell hardnesses of high-purity beryllium (Pechiney SR) as a function of the mean grain size [74].

19.10 Alloys

Beryllium-rich alloys have little industrial importance. The motivation for industrial research on beryllium alloys [10, p. 555; 12, p. 179; 15, pp. 601, 634; 17, p. 103; 132; 166–174] is not great because the solubility of most elements in solid beryllium is low (≈ 1 mol%), and only copper, nickel, cobalt, iron, silver, and platinum have solubilities between 1 and 10 mol%, even at elevated temperatures. In addition, most metals form intermetallic compounds with beryllium [25, 77–79], and these intermetallics are usually quite brittle.

The only alloy containing large amounts of beryllium is Lockalloy [169], which is produced by powder metallurgy and contains 38% Al. Aluminum does not form any beryllides. Therefore, this alloy contains beryllium grains embedded in the ductile aluminum phase with a more or less uniform distribution. This combination has a comparatively high modulus of elasticity (E), low density, and comparatively useful deformation behavior at room temperature. In addition, the notch sensitivity is lower than that of commercial beryllium (Table 19.8) [17, p. 103; 173]. However, Lockalloy has found only limited commercial use.

Table 19.8: Mechanical properties of powder-metallurgy Lockalloy [169] and beryllium-titanium composite materials (extruded powder mixtures [174]).

	ρ , g/cm ³	σ_p , MPa	E , MPa	δ , %	$\sigma_{0.2}$, MPa
Lockalloy	2.09	386	200 000	≈ 10	255
60 vol% Ti	3.4	1100	175 000	5	≈ 770
40 vol% Ti	2.85	829	215 000	2.5	≈ 580

Composite materials made of beryllium and titanium have been developed for use, e.g., as compressor blades in gas turbines [174]. At present, these materials are the only composite materials that allow definite plastic deformation, are impact resistant, and offer the choice of secondary cold or hot working (Table 19.8). Furthermore they can be used to a limited extent even at 400–500 °C.

Beryllium is used as an alloying component in a number of age-hardening alloys [6] based

on copper, nickel, cobalt, and/or iron [10, pp. 24, 49; 175–179]. Small amounts of beryllium improve the castability and oxidation resistance of aluminum and magnesium alloys [180–187]. These alloys are described under the principal component.

Table 19.9: Physical properties of beryllium oxide and carbide [7; 8; 10, p. 599; 11; 12, p. 267; 37; 189, 190].

	BeO	Be ₂ C
Structural type	ZnS	CaF ₂
Melting point, °C	2300–2570	≈ 2400
Density, g/cm ³	3.01	≈ 2.3
Modulus of elasticity, MPa	370 000	320 000
Linear coefficient of thermal expansion, K ⁻¹	5 × 10 ⁻⁶	5.8 × 10 ⁻⁶
Specific heat, Jg ⁻¹ K ⁻¹		
60 K	0.029	
292 K	1.00	1.4
1173 K	2.04	
Thermal conductivity, Wm ⁻¹ K ⁻¹		
room temperature	264	24
673 K	92	
1073 K	29	
Electrical resistance, Wm		
room temperature	10 ¹⁶	1.1 × 10 ⁻²
1273 K	8 × 10 ¹¹	0.45 × 10 ⁻²
2373 K	8 × 10 ⁶	
Compressive strength, MPa	800	720
Bending strength, MPa	285–380	91–98
σ ₂ , fm ²	0.9	2.3
Σ ₂ , cm ⁻¹	0.00066	0.0011
σ ₃ , fm ²	990	1690
Σ ₃ , cm ⁻¹	0.72	0.81

19.11 Compounds

Most beryllium compounds are important only in the production of beryllium metal, and these aspects are described earlier in this article.

Beryllium oxide, BeO, is obtained directly from beryllium hydroxide by calcination or from the basic carbonate, acetate, or sulfate by ignition [11]. The white, reactive powders differ in grain size, morphology, and impurity content [188]. They are used in the production of beryllium oxide ceramics, some of which have most unusual properties (Table 19.9). These ceramics are being used to an ever increasing extent [20].

Beryllium oxide is extremely stable [37]. However, its stability depends on its structure and is determined by the content of bound water. The higher the calcination temperature the more inert the beryllium oxide.

Beryllium nitride, Be₃N₂, is formed by heating beryllium in dry nitrogen in the presence of 2–6% hydrogen (700–1400 °C) or ammonia (1000 °C) [10, p. 570]. Moldings are produced by nitration of beryllium powder in porous molds by hot pressing the nitride at 1800–1900 °C. Relative densities up to almost 100% are achieved in this way. Beryllium nitride is stable in dry oxygen up to 500 °C, but in the presence of water vapor it reacts at lower temperatures. Beryllium nitride is cubic at room temperature, converting to hexagonal at 1400 °C. Two other nitrides, Be(N₃)₂ and BeN, and two beryllium silicon nitrides, Be₄SiN₄ and BeSiN₄, are known. These ternary nitrides are very hard, extremely inert, and stable up to 1850 °C [191].

Beryllium carbide, Be₂C, cubic, is obtained by direct reaction of solid or liquid beryllium with carbon or by reaction of beryllium oxide with finely divided carbon at 2080 °C [7; 10, p. 570]. Moldings are produced by hot pressing the carbide powder in graphite molds at 1800–1950 °C and 7–35 MPa. Beryllium carbide hydrolyzes very readily, even at room temperature, to form beryllium oxide and methane. At high temperatures it is not stable in air. Beryllium carbide vaporizes and decomposes in a vacuum above 2100 °C. The properties given in Table 19.10 are reference values because the beryllium carbide grades which were tested had indefinite structure. The nuclear properties of beryllium carbide are favorable. Beryllium borocarbide is extremely hard and is formed by melting mixtures of beryllium oxide, boron, and carbon in an electric arc.

Beryllium hydride, BeH₂, is a very light (ρ 0.58 g/cm³), white powder at room temperature that is difficult to prepare. It dissociates into beryllium and hydrogen at ≈ 130 °C [37]. Beryllium hydride is of interest as a high-energy solid fuel.

Beryllium hydroxide, Be(OH)₂, is obtained as a white voluminous precipitate on addition of bases to beryllium salt solutions. The fresh precipitate dissolves in sodium and potassium hydroxide and ammonium carbonate solution, but it ages quickly and becomes less and less soluble. The hydroxide also dissolves in aqueous BeSO₄ to form basic sulfates.

Basic beryllium carbonate, BeCO₃·nBe(OH)₂, n = 2–5, is formed in the reaction of beryllium salt solutions with alkali-metal or ammonium carbonate solutions. If excess ammonium carbonate is used, then a readily filtered precipitate of variable composition is formed on boiling. This salt is a suitable starting material for the preparation of beryllium salts of all types. Gentle calcining causes ammonia to escape, leaving beryllium oxide.

Beryllium nitrate, Be(NO₃)₂·4H₂O, is obtained by dissolving pure hydroxide or gently calcined, pure basic carbonate in nitric acid and concentrating the solution until crystallization takes place. Concentrated solutions are also commercially available. The nitrate is sometimes used in the incandescent gas mantle industry for stiffening mantles.

Beryllium sulfate, BeSO₄·4H₂O, is obtained by heating beryllium oxide with sulfuric acid. The tetrahydrate crystallizes from the aqueous solution in well-developed crystals. It can be obtained in very pure form by this method. The tetrahydrate is stable in air, can be dehydrated at about 400 °C, and decomposes above 600 °C to sulfur trioxide. The aqueous solution can dissolve considerable quantities of BeO to form basic sulfate. The sulfate is important chiefly for the recovery of beryllium.

Beryllium fluoride, BeF₂, is a white, freely soluble, low-melting salt. Molten beryllium fluoride is a poor electrical conductor due to the its covalent character. (See Section 19.7.3 for production of BeF₂.) In addition to its use as an intermediate in the preparation of beryllium, it is also sometimes used as an additive to welding and soldering fluxes because it dissolves metal oxides readily.

Beryllium chloride, BeCl₂, crystallizes in asbestos-like matted needles. It is extremely hygroscopic, forming a tetrahydrate. Its reaction with water is intensely exothermic and is accompanied by the release of HCl vapor. Beryllium chloride melts at 416 °C, boils at 520 °C, and, like the fluoride, is a poor electrical conductor in the molten state. (See Section 19.7.3 for production of BeCl₂.) Its principal uses are as the raw material for the electrolytic production of beryllium and as the starting material for syntheses of organoberyllium compounds.

Beryllium bromide, BeBr₂, melts at 490 °C. It is obtained as white needles by the reaction of bromine with a mixture of beryllium oxide and carbon. It is used in organic syntheses.

Beryllium orthophosphate, Be₃(PO₄)₂·6H₂O, is obtained by reaction of beryllium salts with disodium phosphate or diammonium phosphate in acetic acid solution. Its solubility is very low at room temperature but increases sharply with temperature.

Beryllium ammonium phosphate, NH₄BePO₄, whose composition varies greatly due to partial separation of beryllium hydrogen phosphate, is sparingly soluble. Freshly precipitated NH₄BePO₄ is amorphous.

Aqueous beryllium perchlorate, Be(ClO₄)₂, is a solvent for cellulose.

Basic beryllium acetate, a hexaacetato complex, Be₄O(CH₃COO)₆, like the acetylacetate and a few other organic beryllium compounds can be distilled without decomposition. Insoluble in water, it melts at 280 °C and boils at 331 °C. The organic beryllium compounds are being used to an increasing extent as intermediates in the purification of beryllium.

Beryllides of some transition metals are promising structural materials or protective coating materials for high-temperature applications because of their low density, high melting point, good mechanical properties, and resistance to oxidation, even up to high temperatures (Table 19.10) [192–197].

Table 19.10: Properties of some beryllides [193] (RT = room temperature).

Beryllide $m\mu$, K	Oxidation in air, 10 ⁻³ mm in 100 h		Coefficient of thermal expansion, 10 ⁻⁶ K ⁻¹		Thermal conduc- tivity, W m ⁻¹ K ⁻¹		Bending strength, MPa		Modulus of elasticity, 10 ⁴ MPa		Strain at failure, %		Compressive strength, MPa	
	1640 K	1750 K	RT-1790 K	1750 K	1750 K	1750 K	RT	1640 K	1790 K	RT	1640 K	1790 K	RT	1640 K
NbBe ₁₂	1960	22	50	16.8	107.5	152	276	152	31.4	17.2	0.1	1.0	2.4	1380
Nb ₂ Be ₁₇	1980	15	47.5	15.9	112	214	434	248	29.6	17.2	0.1	2.0	≈ 7	—
Nb ₂ Be ₁₉	≈ 1980	—	—	—	—	206	448	186	—	—	0.1	2.0	3.0	—
TaBe ₁₂	2130	12.5	22	15.1	123	214	296	179	31.0	13.8	0.1	1.1	2.6	1030
Ta ₂ Be ₁₇	2265	7.5	22	15.7	—	206	386	241	31.0	13.8	0.1	2.6	≈ 5	—
ZrBe ₁₃	2200	12.5	32.5	17.7	119	172	255	172	32.4	13.8	0.05	0.25	0.6	1310
Zr ₂ Be ₁₇	2260	12.5	30	15.1	—	172	276	241	31.0	13.8	0.1	0.3	0.1	482

19.12 Chemical Analysis

The quantitative determination of beryllium, even in very small amounts, is especially important because of the toxicity of beryllium [155, 198]. The best method is atomic absorption spectrometry. When an acetylene/nitrous oxide flame is used, even beryllium oxide is excited, and it is possible to analyze any solution or dispersion without preliminary treatment [155, 199, 200]. Other methods [201–205] have also been described.

19.13 Storage, Transportation, Legal Aspects

Solid parts and structures made from beryllium metal, alloys, and ceramic beryllium can be stored and transported safely without special precautions as long as neither vapor nor dust is generated. Beryllium and beryllium oxide powder have to be handled with care, as is described in Section 19.8. For storage and transportation of the powders, sealed, unbreakable containers and proper instructions are a necessity.

Because beryllium is used mainly in military, nuclear, aeronautical, and rocket technologies, its trade is restricted. A special license is necessary for export from the United States.

19.14 Uses of the Metal

The properties of beryllium, especially the mechanical properties, are strongly affected by even small amounts of additives, e.g., 1000 ppm or less, and in this sense even commercial grades of beryllium (Table 19.5) represent alloys. The crucial advantage of beryllium over other materials is its combinations of favorable properties. Detailed discussions of the relationship between properties and uses have been published [19, 41].

Table 19.11: World production of beryl (t).

	1975	1976	1977	1978	1979 ^a	1980 ^a	1981 ^b	1982 ^b	1984	1989 ^c	1990	1991 ^a	1992 ^a	1993 ^c
Argentina	303	123	182	24	13	34	33	29	NA ^d	32	34	34	34	35
Brazil	770	406	547	815	498	606	894	882	878	900	850	850	850	850
China ^{e, f}	—	—	—	—	—	—	—	—	—	54	55	55	—	—
Kazakhstan	—	—	—	—	—	—	—	—	—	—	—	—	100	100
Madagascar	—	—	17 ^c	12	11	11	10	11	NA	32	—	—	—	—
Mozambique	9	—	NA	NA	31	22	20	17	—	—	—	—	—	—
Portugal	—	—	—	—	6	21	20	21	—	—	—	—	—	—
Rwanda	20	51	60 ^c	64	51	119	100	110	—	—	—	—	—	—
South Africa	3	3	3	4	1	—	134	66	—	—	—	—	—	—
Uganda ^c	—	60	50	—	—	—	—	—	—	—	—	—	—	—
USA ^f	—	—	—	—	—	—	—	—	—	4566	4548	4339	4826	4939
USSR ^c	1760	1820	1870	1930	2000	2000	2000	2000	NA	1770	1600 ^g	1300 ^g	1100 ^h	800 ^h
Zimbabwe	70	70	114	39	31	10	46	22	NA	28	28	29	23	23
Others	135	20	1	—	6	21	20	NA	—	—	36 ⁱ	15 ⁱ	19 ⁱ	19 ⁱ
Total	3070	2553	2844	2888	2642	2823	3254	3158	878	7382	7151	6622	6952	6766

^aRevised.

^bPreliminary.

^cEstimated.

^dNA = not available.

^eWorld mined beryllium production ($\times 10^3$ t containing Be).

^fMine shipments, incl. bertrandite ore, calculated as equivalent to beryl containing 11% BeO.

^gUSSR/CIS.

^hRussia.

ⁱIncl. Madagascar, Namibia, Nepal, Portugal, South Africa.

The low density of beryllium combined with its high strength, high melting point, and resistance to oxidation is the basis for its use in structural parts that must be light and are exposed to inertial or centrifugal forces. In addition, it has a high modulus of elasticity, which gives light-weight components a high degree of rigidity [19]. Another area of use is in so-called dimensionally stable parts, in which high microyield strength and good thermal conductivity and reflexivity are exploited. It is an excellent heat sink, and therefore used especially for brake systems of airplanes. Applications in civilian nuclear reactors as reflectors and moderators have not met expectations because of radiation damage. However, its favorable nuclear properties have been exploited in weapons systems and in various physical instruments. Beryllium single crystals are the most efficient material for neutron monochromators. Beryllium foil is widely used as windows in energy-dispersive X-ray analyzers.

19.15 Economic Aspects

Data on production and consumption of beryllium is scanty and incomplete, in most cases because beryllium is used mainly for military and similar purposes. The most complete summary is published annually by the U.S. Bureau of Mines (Table 19.11), but the data mainly concerns mined beryl.

19.16 Toxicology and Occupational Health

Beryllium and its compounds when inhaled in finely divided form dust, fume, or vapor may affect the upper airways and lungs. Contact with water-soluble beryllium salts may cause inflammatory reactions of the skin. Beryllium metal, alloys, and ceramic beryllium can be handled safely without special precautions as long as the fabrication process does not require high temperatures or produce particles smaller than 10 μ m.

Prior to 1950, many cases of acute chemical bronchitis, pneumonitis, and contact dermatitis had occurred from high exposures to

water-soluble beryllium salts because the potentially harmful effects of beryllium were insufficiently known. During the same period, numerous cases of *chronic beryllium disease* from exposures to beryllium oxide and metal dusts were reported among production workers, members of their family, and others living close to the plants. Strict exposure control introduced in 1950 succeeded promptly in eliminating neighborhood cases and all forms of the acute disease [206, 207].

However, chronic beryllium disease must still be kept in mind as a potential hazard associated with the basic production and fabrication of beryllium materials. *Metallic beryllium* and *beryllium oxide*, when inhaled as dust, represent the greatest risk; chronic cases have also been reported from inhalation of *beryllium-copper particles* in the form of fine dusts or fumes.

In contrast with other pneumoconioses, chronic beryllium disease is highly selective, because even under the most severe exposure conditions never more than 2% of all workers were affected. The reason for this epidemiological peculiarity is an allergy-like immune reaction that occurs only in a very small portion of the population. The actual cause of this predisposition is not yet fully understood, nor can it be predetermined. Therefore, strict exposure control is needed for all individuals at risk. Any process likely to generate respirable particles of beryllium, such as grinding, polishing, and buffing of metallic beryllium, beryllium oxide, or beryllium alloys, must be considered as potentially harmful and requires adequate venting. Special attention is indicated for beryllium copper because the vapor pressure of beryllium is greater than that of copper.

Cold rolling, drawing, stamping, and slitting generally produce no or very few fine particles and are unlikely to cause atmospheric beryllium concentrations in excess of the exposure limits. The same is true for drilling and sawing with the use of liquid coolants, if the appropriate precautions are taken. Dry sawing and drilling with fine tools usually generates

fairly large amounts of respirable dusts, and proper venting equipment must be installed.

Beryllium in the Body [208]. Upon ingestion, beryllium metal, oxide, or alloys do not exert harmful effects on the intestinal mucosa and are not absorbed to any significant degree. Absorption through the skin is also minimal and without clinical consequences. Beryllium-containing particulates, if inhaled in low concentrations, will be removed from the alveolar spaces by macrophages and eliminated from the airways via mucociliary escalation. Amounts exceeding the capacity of this mechanism will be transported into the lung tissue and from there gradually into bone, liver, and kidney tissues. Because of a very slow elimination from the body, the biological half-life is long. In most individuals beryllium is removed from these storage organs and excreted via the kidneys without any harmful effect.

Clinical Symptoms [208, 209]. Only in individuals predisposed to sensitization can the inhalation of excessive beryllium lead to *chronic beryllium disease* (also known as *beryllitis*), an inflammatory process involving the connective tissues of the lungs. However, latent periods of 5–25 years may precede the manifestation of the disease — shortness of breath on exertion; chronic, dry cough; and burning substernal pain. A gradual reduction in lung volume caused by replacement of the normal lung structures by scar tissue and interference with gas exchange between alveolar air and blood are the primary causes of these symptoms. Their extent may show great variations. Approximately one third of all affected individuals have relatively little incapacitation and a normal life expectancy. At the other end of the spectrum, marked scarring and shrinkage of the lung tissue may cause a severe chronic strain on the right heart chamber and serious physical impairment.

Because it shares many features with other lung diseases, the accurate diagnosis of chronic beryllium disease is difficult. It requires a reliable exposure history and, in addition to chest X-rays and pulmonary function evaluation, a lymphoblast transformation test,

really the only specific proof of the disease [207, 208].

Corticosteroids are helpful in therapy. Although they do not cure the disease, they may bring it to a standstill and relieve symptoms. Further exposure to beryllium must be avoided.

Carcinogenicity. Beryllium compounds have produced tumors in several animal species [210, 211]. *Mutagenicity* tests were negative in bacteria and yeasts, but they were positive in cultures of mammalian cells [212, 213]. Regarding *teratogenic* and *reproductive* effects, the presently available information is insufficient for any conclusions. No convincing evidence exists, in spite of forty years of close observation, that beryllium is carcinogenic for humans.

Prevention [207, 209, 211]. In the United States the TLV is $2 \mu\text{g}/\text{m}^3$ as a daily weighted average with a 30-min peak of $25 \mu\text{g}/\text{m}^3$. Beryllium is classified in group A2 (suspected of carcinogenic potential in humans) by ACGIH. In Germany, beryllium is also classified as an A2 material and a TRK of $5 \mu\text{g}/\text{m}^3$ for grinding of beryllium metal and alloys and $2 \mu\text{g}/\text{m}^3$ for all other compounds was established (1983).

No new cases of chronic beryllium disease have developed whenever atmospheric beryllium levels were kept consistently at or below these levels. However, inhalation of high concentrations of beryllium during very short periods has also resulted in chronic beryllium disease. For that reason duration and concentrations of the short-term exposure limit of $25 \mu\text{g}/\text{m}^3$ must not be exceeded.

Ore extraction and production of beryllium metal, oxide, and alloys present the greatest risk for excessive exposures: here the most efficient venting equipment and shop-laundered work clothes are required. Melting and welding of beryllium alloys also belong to this category.

Cutting, milling, or turning of beryllium metal or alloys produce significantly less respirable particles, and the concentration in the shop air can be readily kept at or below 1

$\mu\text{g}/\text{m}^3$ with the help of source exhaust systems. Many fabricating operations for beryllium alloys and ceramic oxide generate such low breathing zone and ambient air concentrations that special venting may not be needed. In those instances ordinary shop coats are sufficient.

Medical surveillance [207, 208] should include chest X-rays and spirometry prior to employment, annually, and on termination. For minimum exposure risks, less frequent intervals may be satisfactory.

19.17 References

The following abbreviations are used in the citations.

- AERE Atomic Energy Research Establishment
- AIME American Institute of Mining, Metallurgical, and Petroleum Engineers
- AMC American Motor Co.
- ASD Avco Systems Division
- AWRE United Kingdom Atomic Research Authority, Atomic Weapons Research Establishment
- BBC Brush Beryllium Co.
- DMIC Defense Metals Information Center, Battelle Memorial Institute
- FIRL Franklin Institute Research Laboratories
- GEC General Electric Co.
- NASA National Aeronautics and Space Administration
- NMAB National Materials Advisory Board
- NMI Nuclear Metals Inc.
- RFP The Dow Chemical Co., Rocky Flats Division
- SAE Society of Automotive Engineers
- UCRL University of California, Lawrence Radiation Laboratory
- USAEC United States Atomic Energy Commission
- WADC Wright Air Development Center
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20 Magnesium

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20.1 Introduction

Magnesium is a silvery white metal; it has a valence of two, and its configuration is $1s^2 2s^2 2p^6 3s^2$. The crystal structure is dense hexagonal; lattice constants at 20 °C are $a = 0.32$ nm, $c = 0.52$ nm. The element has an atomic number of 12 and belongs to group 2A of the periodic table. It occurs as three isotopes: ^{24}Mg (78.70%), ^{25}Mg (10.13%), and ^{26}Mg (11.17%).

20.2 History

Metallic magnesium was first isolated by DAVY in 1808, via electrolysis of anhydrous

magnesium chloride with a mercury cathode. Bussy extracted the metal in 1828 by reducing fused magnesium chloride with metallic potassium vapor. In 1833 FARADAY electrolyzed dehydrated liquid magnesium chloride to form liquid magnesium and chlorine gas. The first industrial production of magnesium by electrolysis of molten carnallite began in 1886 in Hemelingen (Germany).

In 1940 L. M. PIDGEON pioneered the first industrial metallothermic magnesium extraction plant in Canada; it was based on early German patents in which dolomite was reduced with ferrosilicon under vacuum [1].

Table 20.1: Mechanical properties of magnesium at 20 °C.

	Tensile strength, MPa	Tensile yield strength (0.2%), MPa	Compressing yield strength (0.2%), MPa	Elongation ^a , %	Brinell hardness ^b
Sand cast, thickness 13 mm	90	21	21	2–6	30
Extrusion, thickness 13 mm	165–205	69–105	34–55	5–8	35
Hard rolled sheet	180–220	115–140	105–115	2–10	45–47
Annealed sheet	160–195	90–105	69–83	3–15	40–41

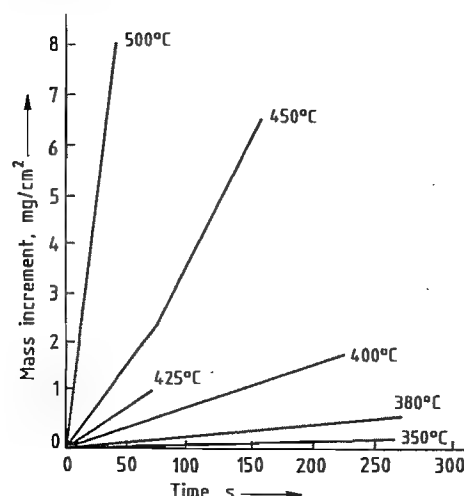
^a In 50 mm.^b With 500-kg load, 10-mm diameter ball.

Figure 20.1: Rate of oxidation of magnesium in moist air [22].

20.3 Properties

Physical properties of magnesium follow (see also [2]):

<i>mp</i> [3]	650 ± 2 °C
<i>bp</i> [3]	1107 ± 10 °C
Latent heat of fusion [4]	0.37 MJ/kg
Latent heat of evaporation [5]	5.25 MJ/kg
Heat of combustion [4]	25.1 MJ/kg
Specific heat [3]	
at 20 °C	1030 J kg ⁻¹ K ⁻¹
at 600 °C	1178
Electrical resistivity at 20 °C [3]	4.45 μΩ·cm
Thermal conductivity at 25 °C [4]	155 W m ⁻¹ K ⁻¹
Linear coefficient of thermal expansion [3]	
at 20 °C	25.2 × 10 ⁻⁶ K ⁻¹
at 20–300 °C [5]	27–28 × 10 ⁻⁶
Density (solid) [4]	
at 20 °C	1738 g/cm ³
at 600 °C	1622
Density above 650 °C (liquid) [6]	1.834 – 2.647 × 10 ⁻⁴ T g/cm ³
Standard redox potential [6]	–2.372 V

Mechanical properties of magnesium are listed in Table 20.1. Its dynamic modulus of elasticity is 45 GPa, and its static modulus of elasticity 43 GPa. Pure magnesium is not used for commercial structural applications although the metal has a high damping capacity and is easily machined and formed into shapes by casting or hot forming processes [3].

Chemical Properties. Magnesium burns in air with an intense white flame. The ignition temperature is 645 °C in dry air but decreases with increasing moisture content [5]. The rate of oxidation in moist air at different temperatures is illustrated in Figure 20.1 [7]. Burning magnesium reacts violently with water. Fire is extinguished with magnesium chloride, alkali chlorides, dry sand, or dry iron sponge. Magnesium reacts with gaseous chlorine to form magnesium chloride and with nitrogen at ca. 500 °C to form Mg₃N₂.

Pure magnesium has a high resistance to corrosion because its galvanic activity is low. Contamination with heavy metals (usually copper, iron, and nickel), chlorides, and oxide or nitride inclusions combined with exposure to chloride-containing solutions on untreated surfaces, strongly promote corrosion due to enhanced galvanic activity. The metal is readily dissolved by most organic and inorganic acids. A protective layer of water-insoluble magnesium hydroxide is formed when magnesium is exposed to moist air or clean water at room temperature. Magnesium is resistant to alkali hydroxide solutions, hydrofluoric acid, fluorine, and fluorine compounds (including ammonium hydrogen difluoride) due to the formation of protective hydroxide and fluoride films.

The ability of magnesium to form stable protective oxide, chromate, phosphate, sulfate, and fluoride films is employed commercially in protective coating systems used as primers for paints or as final coatings. The behavior of magnesium against various chemicals is listed in [8, p. 575].

20.4 Raw Materials [9, 10]

Magnesium is the eighth most abundant element in the earth's crust (average magnesium content, 2.1%). Magnesium does not occur in nature in elemental form but in the form of compounds in seawater, minerals, brines, and rocks. The element is enriched in ultrabasic rocks.

The prime raw material sources for magnesium extraction are the minerals dolomite (CaCO₃·MgCO₃), magnesite (MgCO₃), and brucite [Mg(OH)₂]; magnesium-rich salts such as carnallite (MgCl₂·KCl·xH₂O), kieserite (MgSO₄·H₂O), bischofite (MgCl₂·6H₂O), kainite (KCl·MgSO₄·3H₂O), and langbeinite (K₂SO₄·MgSO₄); and magnesium-rich brines and seawater. High-quality magnesites contain: MgO 45–47%, CaO 0.5–1.2%, SiO₂ 0.1–0.15%, Al₂O₃ and Fe₂O₃ 0.1–0.6%, Mn 20–500 ppm, Ni 2–300 ppm, B 10–60 ppm. Magnesium-rich brines are obtained as by-products from potash production or from surfacial or underground brine deposits. Analyses of dolomites and brines used for magnesium extraction are given in Tables 20.2 and 20.3, respectively.

Magnesium silicates such as olivine [Mg·Fe(SiO₄)₂] and forsterite (Mg₂SiO₄) have not been used so far for magnesium extraction.

Table 20.2: Composition of dolomites (%).

Deposit	MgO	CaO	Fe ₂ O ₃ + Al ₂ O ₃	SiO ₂
Serfold, Norway	21.2	30.4	0.1	1.3
Tochigi, Japan	17.4	35.1	0.5	0.15
Addy, Washington	20–21.8	30–31.5		1.5
Marignac, France	19–20	32–34	0.3–0.5	0.2–0.4
Haley, Canada	21.3	30.7	0.1	0.15

Table 20.3: Composition of brines (%).

Brine	Mg ²⁺	Na ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻
Great Salt Lake ^a	1.1	7.6	0.02	14.1	2.0
Dead Sea	3.4	3.3	1.4	17.5	0.7
Seawater	0.13	1.08	0.04	1.94	0.27
"Edelsole", Kali und Salz AG	8.5	0.2		25	0.24

^a Composition is subject to seasonal and long-term variations.

Total world production of magnesium in 1988 was ca. 240 × 10³ t, of which 42% came from dolomite, 36% from salt or brine deposits, 18% from seawater, and 4% from magnesite. Recent plants in Canada increased the share of magnesite.

20.5 Production

Magnesium is produced commercially by electrolysis of magnesium chloride melts and by metallothermic reduction of magnesium oxide with silicon. A wide variety of processes are used. The extraction of magnesium by electrolysis consists of two steps: (1) preparation of the magnesium chloride cell feed and (2) electrolysis. All extraction processes are followed by refining and casting.

Electrolysis of magnesium oxide dissolved in fused fluorides has also been considered. However, the solubility of magnesium oxide in the electrolyte is low, and practical solutions for metal collection have not been found. For further details, see [11]. Composite MgO–C anodes have been tested in fluoride, fluoride–chloride, and chloride electrolytes on a laboratory scale [12].

Electrolysis of magnesium chloride in aqueous solution liberates hydrogen, not magnesium, at the cathode. Attempts to electrolyze magnesium salts in organic solvents have not been successful.

Carbothermic reduction of magnesium oxide is not used industrially. The main problems are high reaction temperature (1800–2000 °C) and rapid cooling of reaction gases to suppress magnesium oxide formation [13]. Recent experimental studies have been based on rapid adiabatic expansion of the gases or cooling in liquid metal [14]. Attempts to en-

hance selectivity of the reduction step in the carbothermic reduction of magnesium oxide in molten $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{MgO}$ slag have been reported [15].

20.5.1 Extraction by Electrolysis

20.5.1.1 Preparation of Magnesium Chloride Cell Feed

Magnesium chloride cell feeds in industrial use consist of dehydrated $\text{MgCl}_{2(s)}$ or $\text{MgCl}_{2(l)}$; dehydrated carnallite $\text{MgCl}_2 \cdot \text{KCl}_{(s)}$; or $\text{MgCl}_2 \cdot 1.5\text{H}_2\text{O}_{(s)}$. Cell feeds contain 3–8% alkali chlorides and minor impurities of C, SiO_2 , MgO , SO_4^{2-} , B, and heavy-metal compounds. Alkali chlorides accumulate in the electrolytic cell as major constituents of the electrolyte. Metallic and nonmetallic impurities are undesirable because they adversely affect cell performance and the corrosion resistance of magnesium.

The use of pure dehydrated magnesium chloride allows coproduction of highly concentrated chlorine gas and electrolysis at high current efficiencies. Dehydrated carnallite (which contains only 50% MgCl_2) leads to accumulation of significant tonnages of potassium-rich electrolyte in the electrolysis. The impurity level of Russian carnallite, the only carnallite cell feed in use, is high and increases power consumption in electrolysis. The chlorine concentration is high. The water content of $\text{MgCl}_2 \cdot 1.5\text{H}_2\text{O}$ results in high consumption of anode carbon and formation of sludge in the cell; power consumption is high.

Dehydration of Magnesium Chloride

The two main routes to the production of dehydrated magnesium chloride cell feed are: (1) chlorination of magnesia (MgO) or magnesite (MgCO_3) in the presence of carbon or carbon monoxide and (2) dehydration of aqueous magnesium chloride solutions (brines) or hydrous carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$).

Dissolution of magnesium chloride in ethylene glycol with subsequent dehydration and

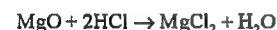
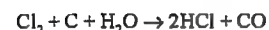
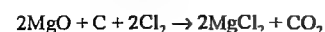
regeneration of the alcohol via a complex magnesium chloride ammonia compound has been suggested [16]. The process has not, however, been used industrially.

Chlorination of Magnesia and Magnesite

Two principal processes are used industrially to chlorinate magnesia and magnesite: (1) the IG Farben process presently in operation at Norsk Hydro's Porsgrunn plant and (2) the MagCan process under installation in Alberta, Canada.

IG Farben Process (Figure 20.2). In the process used by Norsk Hydro, caustic magnesium oxide (lightly burned) extracted from seawater, is mixed with charcoal and magnesium chloride brine on a rotating disk to form pellets with a diameter of 5–10 mm. Hydrated magnesium oxide and magnesium oxychlorides act as binders. After slight drying, pellets containing ca. 50% magnesium oxide, 15–20% magnesium chloride, 15–20% water, 10% carbon, and a balance of alkali chlorides are conveyed to the chlorinators (Figure 20.3).

The lower third of the brick-lined cylindrical shaft furnace is filled with carbon blocks (c) that act as resistors and are heated by carbon electrodes (e). Chlorine produced during subsequent electrolysis of magnesium chloride is introduced in the resistor-filled zone. The charge (b) resting on the resistor bed reacts with chlorine at 1000–1200 °C. The main reactions are:



The reaction mechanism is complex and involves further side reactions. Chlorinator-grade magnesium oxide is processed for minimum impurities and high surface area. Molten magnesium chloride collects in the bottom of the furnace from where it is tapped and transported to the electrolytic cells in sealed containers.

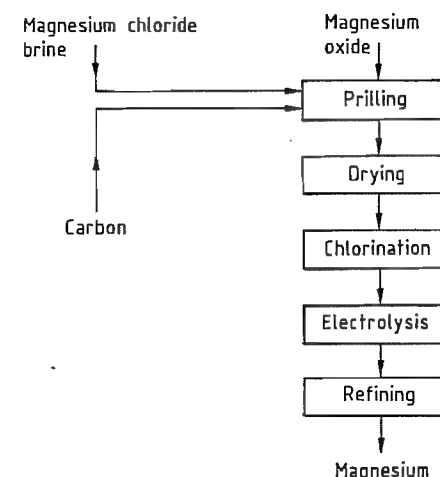


Figure 20.2: Flow sheet for production of magnesium via chlorination of magnesia (Norsk Hydro).

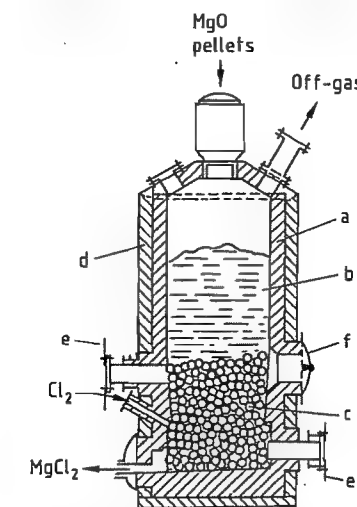


Figure 20.3: The IG chlorinator: a) Refractory material; b) Charge; c) Carbon resistors; d) Steel mantle; e) Carbon electrodes; f) Door for slag removal.

Off-gases at 100–200 °C containing air, CO , CO_2 , traces of HCl , Cl_2 , SO_2 , H_2S , and chlorinated hydrocarbons are scrubbed; the wash water is then filtered and chemically treated in several stages before release to stack and sewers. Slag rich in magnesium silicate formed due to the presence of silica in the magnesia is removed at intervals.

The magnesium yield is ca. 90%, and the carbon consumption is 0.45 t per tonne of

magnesium. Magnesium chloride solution added to the charge compensates for chlorine losses. The anhydrous MgCl_2 product typically contains less than 0.1% MgO , 0.1% C, 0.1% SiO_2 , and 20 ppm B. Each chlorinator has an equivalent annual magnesium production capacity of 1800–2000 t.

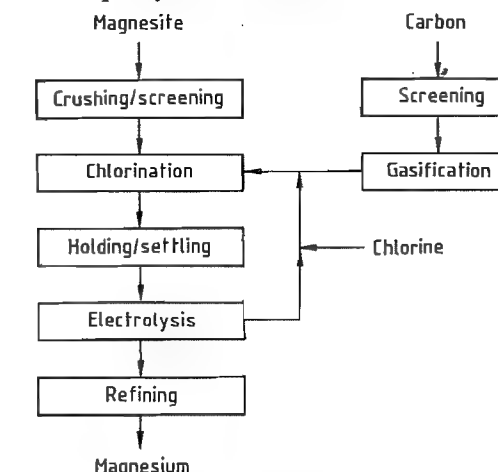
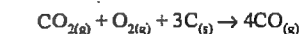
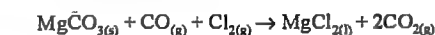


Figure 20.4: Flow sheet for production of magnesium via chlorination of magnesite (MagCan).

MagCan Process (Figure 20.4). Natural magnesite from British Columbia is crushed and screened. Magnesite fines with a particle size < 6 mm are disposed as solid waste. The coarse material is charged at intervals to a reactor of the same general description as the IG shaft furnace (Figure 20.3). Chlorine from the electrolysis is mixed with fresh makeup chlorine and carbon monoxide from a gas generator. It is then fed into the lower section of the reactor where it reacts with preheated magnesite resting on a bed of carbon resistors. The main reactions are



The magnesite is present in lump form. During the reaction, chlorine and carbon monoxide must penetrate the lumps while magnesium chloride simultaneously drains from the surface [17].

The process is in thermal balance at 1010 °C which is also the temperature in the

reaction zone. Off-gases leaving the top of the reactor at 250–650 °C contain primarily carbon dioxide; small amounts of carbon monoxide; and unreacted chlorine, hydrogen chloride, sulfur dioxide, phosgene, chlorides of aluminum, iron and silicon, and traces of chlorinated hydrocarbons. The off-gases are passed through multistage absorption towers and activated carbon columns to remove residual chlorinated hydrocarbons, sulfur dioxide, chlorine, and phosgene before release to the stack. Part of the cleaned off-gas is mixed with oxygen and recirculated to the gas generator after compression. The gas generators operate on calcined petroleum coke with a particle size > 6 mm. Residual tar and volatile oils in the fresh coke are driven off by the heat of reaction and leave via a separate upper gas offtake.

Liquid process effluents are injected in deep wells after chemical treatment and removal of inert solid material. The latter is deposited as landfill. Off-gases are washed with sodium carbonate and sodium hydroxide. Sodium chloride is removed from the liquid purge streams by passing the solutions over a catalyst. Acidic and alkaline streams are combined to adjust the pH. The resulting liquid is used to dissolve soluble components (mostly chlorides) from liquid wastes and is then filtered and disposed of in an injection well.

Molten magnesium chloride is tapped from the reactors at 800 °C at frequent intervals. During operation, silica-rich slag gradually builds up at the bottom of the magnesite bed, which must eventually be cleaned out. Each reactor is reported to have an equivalent annual production capacity of 1500 t of magnesium. Magnesium chloride containing < 0.2% magnesium oxide is conveyed to melt cells where granular sodium chloride and potassium chloride are added to obtain the desired electrolyte composition. The temperature in the melt cells is adjusted to 700 °C. The cells act as intermediate storage tanks for magnesium chloride and as settling tanks for magnesium oxide and other particulate matter.

The process requires nondecrepitating, high-purity magnesite and consumes ca. 1 t of

chlorine, 0.55 t of coke, 0.5 t of oxygen, and 4.3 t of magnesite per tonne of magnesium. The MagCan process is proprietary and protected by patents [18].

Dehydration of Aqueous Magnesium Chloride Solutions

Brines containing 33–34% of magnesium chloride may be derived as by-product from the potassium industry or produced by dissolving magnesium-bearing minerals in hydrochloric acid (Norsk Hydro process). Naturally occurring dilute brines are concentrated by solar evaporation (National Lead process) or conventional dehydration processes (Dow Chemical process). Unwanted impurities in the brines (e.g., Fe, Ni, SO_4^{2-} , B, Br_2) are removed prior to dehydration. To avoid hydrolysis above 200 °C, the final dehydration is performed in an atmosphere of dry hydrogen chloride.

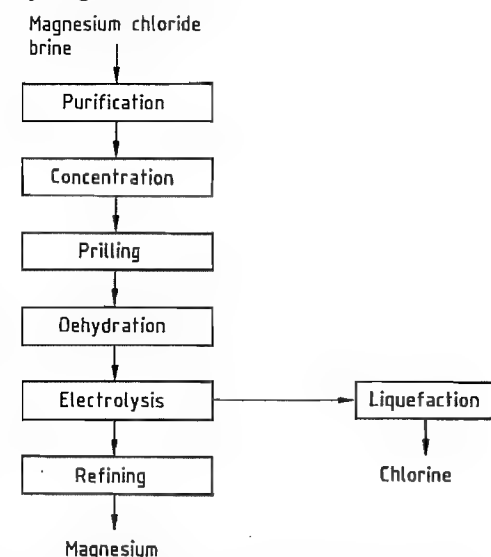


Figure 20.5: Flow sheet for production of magnesium via dehydration of magnesium brine (Norsk Hydro).

Norsk Hydro Process (Figure 20.5). The raw material for magnesium production in Norway is brine from the German potash industry with the following average composition: 33% MgCl_2 , 1.08% MgSO_4 , 0.5% NaCl , and 0.2%

KCl. Feedstock for the Norsk Hydro magnesium plant in Quebec is obtained by dissolving magnesite in hydrochloric acid.

The brine is treated with sodium sulfide, calcium chloride, and barium chloride to remove heavy metals and sulfates by precipitation and filtration. Purified 34% magnesium chloride solution is preheated by process waste heat and concentrated to 45–50% magnesium chloride by steam heat exchangers before prilling. Sizes of the prills are kept within close tolerances, and their shape is controlled to optimize the subsequent dehydration step in fluidized beds employing hot air at 150–180 °C and finally hydrogen chloride gas at 300–400 °C. Water and magnesium chloride dust in off-gases from the hydrogen chloride dehydration step are absorbed in concentrated magnesium chloride solution by extractive distillation. Essentially dry hydrogen chloride gas is preheated and returned to the hydrogen chloride dehydration step. Magnesium chloride prills containing < 0.1% magnesium oxide are transported pneumatically to the electrolysis cells. Magnesium and chlorine recoveries in this continuous, high-volume, closed process are ≥ 97%. The process is proprietary and covered by patents [19].

National Lead Industries Process (Figure 20.6). The National Lead Industries magnesium plant at the Great Salt Lake, Utah, was started in 1972 and is owned and operated by Amax. Seawater containing 0.5–1% Mg, 0.8% SO_4^{2-} , 3% Na, and 0.25% K is concentrated in solar evaporation ponds to precipitate potassium chloride, sodium chloride, and some carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$). The resulting crude brine contains 7.5% Mg, 4% SO_4^{2-} , and < 1% K and Na, and is desulfated with calcium chloride solution generated in the process. The boron content is decreased from 500 to 3 ppm by liquid extraction with kerosene. The brine is preheated before spray drying by direct contact with hot off-gases from the spray dryers. Each spray dryer is connected to a turbine fired with natural gas. Exhaust gases enter the top of the spray dryers at

515 °C. The energy efficiency of this system is ca. 80%.

The resulting spray-dried powder contains ca. 4% water and 4% magnesium oxide. It is melted in an electrically heated, brick-lined melt cell and treated with carbon and chlorine gas to lower the content of magnesium oxide, water, bromine, sulfate, aluminum, and heavy metals. In a second reactor vessel, impurities are further reduced with chlorine gas in the presence of carbon at 830 °C to an average magnesium oxide level of 0.05%. Iron(III) chloride acts as a catalyst in these reactions, forming a complex with magnesium chloride.

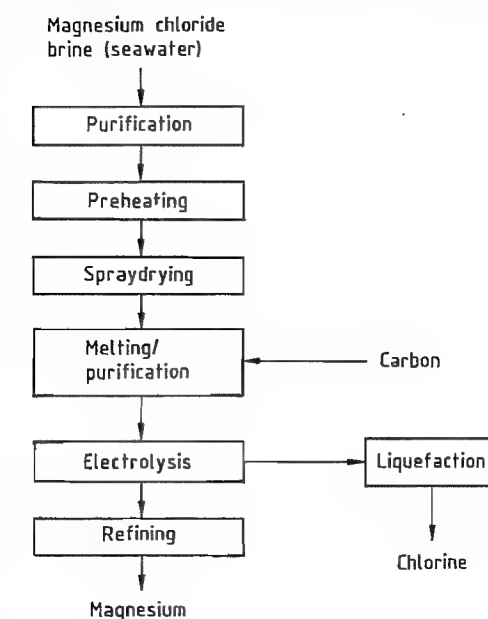


Figure 20.6: Flow sheet for production of magnesium via dehydration of seawater (National Lead Industries).

Off-gases containing chlorine, hydrogen chloride, sulfur dioxide, magnesium chloride dust, and chlorinated hydrocarbons are scrubbed with milk of lime [$\text{Ca}(\text{OH})_2$] to form the calcium chloride used in the desulfation stage. The molten magnesium chloride product is transported to the electrolytic cells in trucks and contains 95% MgCl_2 , < 0.1% MgO , and 0.01% SO_4^{2-} , the balance being alkali chlorides. The process is a net producer of

chlorine (0.5–0.8 t per tonne of magnesium) [20].

Dow Chemical Process (Figure 20.7). Hydrous magnesium chloride ($\text{MgCl}_2 \cdot 1.5\text{H}_2\text{O}$) is used as cell feed by Dow Chemical. Magnesium hydroxide slurry precipitated from seawater with calcined dolomite is dewatered on rotary filters to 8–12% magnesium, dispersed in magnesium chloride solution, and neutralized with hydrogen chloride. Sulfuric acid is added to precipitate excess calcium, which is then removed by filtration. Sulfate ions are adjusted by a proprietary process. The brine is further concentrated to 35% magnesium chloride with waste heat. The purified brine is fed to a dryer where it is concentrated further to 70% magnesium chloride, which is a dry granular solid [21]. Alternatively, the 35% brine can be concentrated directly to 70% solid particles in a spouting bed where the brine is sprayed on solidified particles in an airstream at 180 °C. Undersized particles are separated in cyclones and returned to the dryer.

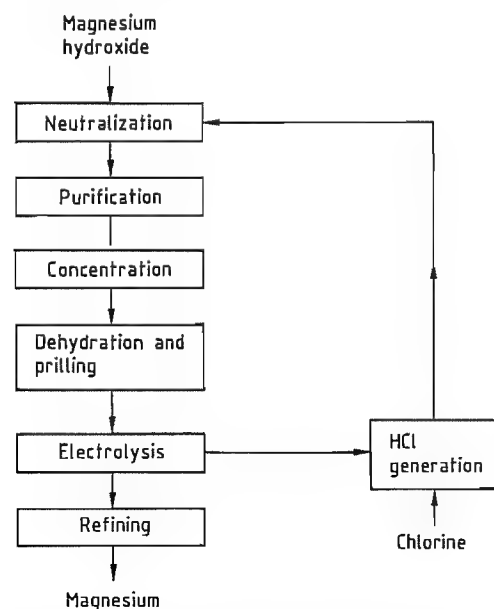


Figure 20.7: Flow sheet for production of magnesium via dehydration of seawater (Dow Chemical).

The hydrogen chloride used for neutralization is partly recovered from the anode gases and partly added to the hydrogen chloride furnaces as makeup chloride in various forms. The Dow process has the potential to produce saleable liquid chlorine when magnesium chloride solutions are used as feedstock.

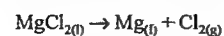
Dehydration of Carnallite

Carnallite cell feed for magnesium production is used only in the former Soviet Union. Carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) is obtained as a natural mineral or as a by-product in the processing of potassium chloride from complex salt deposits. Dehydration of carnallite is simpler than that of aqueous magnesium chloride because hydrolysis is weaker. According to [22], impurities in the carnallite must not exceed the following levels: CaSO_4 0.06%, B 0.001%, Fe 0.01%, and SiO_2 0.01%. The sodium chloride content may be 5–7%.

Carnallite is dehydrated in two stages. The first stage is performed in a fluidized bed at 160–200 °C to give a water content of 3.7–4.8%. The second stage, which yields molten dehydrated carnallite, is performed in a chlorinator at 700–750 °C. The chlorinator combines melting, chlorination, and settling mixing in a single unit. The final product contains 49–51% magnesium chloride and 0.6–1% magnesium oxide. Efforts are being made to reduce the degree of hydrolysis during dehydration and to replace the chlorination stage by hydrogen chloride treatment in a fluidized bed.

20.5.1.2 Electrolysis [7]

Magnesium chloride is electrolyzed in a molten mixture with alkali chlorides at 700–800 °C, the main reaction being



The electrolyte is contained in brick-lined vessels or a steel shell. The magnesium rises to the surface because it is lighter than the electrolyte.

Table 20.4: Composition and properties of electrolytes.

Electrolyte	Composition, %	mp, °C	Properties at 700 °C			
			Density, kg/m ³	Conductivity, S/m	Viscosity, mPa·s	Surface tension, mN/m
Potassium	5–12 MgCl_2 70–78 KCl 12–16 NaCl	650	1600	183	1.35	104
Sodium–potassium	10 MgCl_2 50 NaCl 40 KCl	625	1625	200	1.58	108
Sodium–calcium	8–16 MgCl_2 30–40 CaCl_2 35–45 NaCl 0–10 KCl	575	1780	200	2.22	110
Lithium–potassium	10 MgCl_2 70 LiCl 20 KCl	550	1500	420	1.20	
Lithium–sodium	10 MgCl_2 70 LiCl 20 NaCl	560	1521	488		
Sodium–barium	10 MgCl_2 20 BaCl_2 50 NaCl 20 KCl	686	1800	217	1.70	110
Magnesium		649	1580			

Technical Data

Industrial electrolytic cells differ in electrode configuration, flow pattern of the electrolyte, and collection system for reaction products. Steel cathodes and graphite anodes are arranged vertically or at an angle. Electrodes may be monopolar, bipolar, or a combination of both, with interpolar gaps ranging from 3 to 12 cm and current densities from 2000 to 8000 A/m².

Electrolyte filled with chlorine gas adjacent to the anodes has a lower density than the bulk electrolyte, which results in circulation. The circulating electrolyte carries magnesium globules to the collecting area. Small bubbles of chlorine may follow the flow and escape into the ventilation system [23].

Under operating conditions (10% MgCl_2 and 1000 K) the energy of formation of magnesium is 520.9 kJ/mol, and the enthalpy 597.3 kJ/mol. Consequently, the reversible decomposition voltage is 2.70 V. The thermoneutral voltage ($\Delta H/2F$) is 3.095 V. According to Faraday's law, 4.534×10^{-4} kg of magnesium is formed per ampere per hour.

Under thermoneutral conditions energy consumption is 6.8 kWh/kg. In industrial cells, however, power consumption may range from 10 to 20 kWh/kg; 40–65% of the energy input generates heat as a result of ohmic resistance of the electrolyte and recombination of magnesium and chlorine. Heat generation is necessary to compensate for heat losses from the electrodes and the cell surface. Heat balances for IG cells are reported in [3, 7]. Current efficiencies normally range from 0.75 to 0.95. The main cause of reduced current efficiency is the recombination of dissolved chlorine and magnesium in the electrolyte.

The composition and primary characteristics of electrolytes used in the electrolysis are listed in Table 20.4; they normally contain 8–20% magnesium chloride. Other chlorides (BaCl_2 or LiCl) may be added to influence the density; lithium chloride also increases the conductivity of the melt. The density of the lithium potassium chloride electrolyte is lower than that of liquid magnesium, permitting magnesium to collect at the bottom of the cell. The solubilities of magnesium and chlorine in commercial electrolytes at 730 °C are 0.005%

and $6.27 \times 10^7 \text{ mol/cm}^3$, respectively. Solubilities increase with increasing temperature [24].

Comprehensive measurements of the characteristics of electrolyte compositions and the pure salts are reported in [25]. Excess electrolyte components brought to the cell with the cell feed are removed by pumping into molds or by closed, vacuum-operated containers mounted on trucks. At 750°C the standard decomposition voltages of the electrolyte components are: MgCl_2 2.51 V, NaCl 3.22 V, KCl 3.27 V, LiCl 3.30 V, CaCl_2 3.33 V, and BaCl_2 3.40 V. With magnesium chloride contents below ca. 5%, sodium is deposited; this lowers current efficiency and causes a temperature rise due to recombination of sodium and chlorine.

Impurities in the cell feed disturb cell performance by passivating the cathode surface and hindering the coalescence of metal globules or their free rise to the surface. The upper permissible limits for common electrolyte impurities, in parts per million, follow [26]:

MgO	2000
C	1500
H ₂ O	1000
Mn	600
Fe	200
S	100
Si	100
P	50
B	10

Small additions of calcium fluoride, sodium fluoride, amorphous carbon, and alkaline-earth metals to the electrolyte counteract these undesired effects.

Magnesium chloride and magnesium react with oxygen in air or with oxygen-containing compounds to form magnesium oxide, which has a low solubility in the melt. The oxide can form a layer on the cathode surface, resulting in higher electrical resistance. Magnesium oxide with entrapped electrolyte and magnesium globules form a sludge at the bottom of the cell which must be removed at intervals. The amount of sludge is significantly lower in sealed as opposed to open cell designs.

Theoretically, 2.918 t of chlorine is produced per tonne of magnesium; commercial cells operating with dehydrated magnesium chloride may yield 2.7–2.8 t of chlorine with a

concentration of $\geq 95\%$. The chlorine gas from cells operated on dehydrated cell feed contains small amounts of air, dust from the electrolyte components, and minor amounts of chlorinated hydrocarbons requiring efficient systems for collection and destruction. Electrolytic magnesium contains typically $\geq 99.8\%$ magnesium.

Electrolytic Cells

IG Cell. The cell concept first developed by IG Farben Industrie in Germany in the 1930s is now in operation in the former Soviet Union, China, and the United States. Figure 20.8 illustrates the electrode configuration and the circulation of the electrolyte [26].

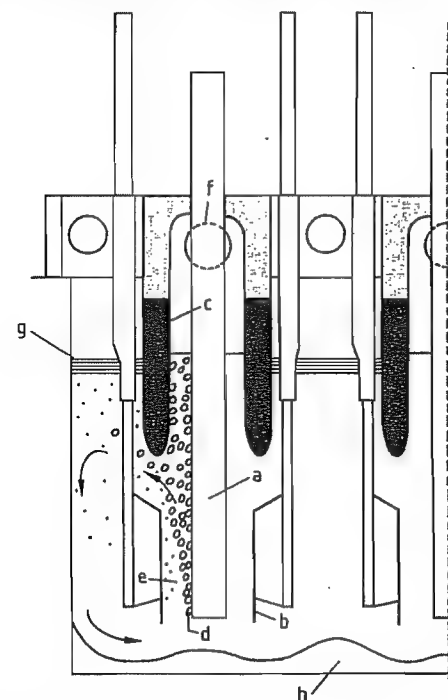


Figure 20.8: Electrode configuration in the IG cell: a) Graphite cathode; b) Steel cathode; c) Semi wall; d) Chlorine bubbles; e) Magnesium globules; f) Chlorine outlet; g) Magnesium; h) Sludge.

The brick-lined cell is divided into four to six compartments by semisubmerged refractory partition walls termed semi walls (c). Three to five water- or air-cooled graphite an-

ode plates (a) are installed and tightly sealed in the refractory cover of the cell. The semi walls on each side of the anodes separate the magnesium metal and the chlorine gas. Steel cathodes (b) are installed in the cathode compartments from above or through the side walls. Cells operated at $750\text{--}780^\circ\text{C}$ have a life of ca. one year, limited by the deterioration of the semi walls. The metal is collected from each of several cathode compartments and chlorine from each anode compartment. Extensive cathode chamber ventilation causes oxygen and water in the ventilation gases to react with metal and electrolyte to form sludge. The current efficiency is typically 0.80–0.85, and the amperage is in the range 60–120 kA. The chlorine concentration may reach 90–95% and is limited by air leaks through the semi walls. Anode consumption is 15–20 kg per tonne of magnesium. Cell regularity (days in operation divided by total days available) is 95–98% of available time, and the power consumption per tonne of magnesium is 16–18 MWh when operated on molten magnesium chloride. For further details of the IG cell, see [27].

Norsk Hydro Cell. This cell has been in operation since 1978 and consists of a sealed, bricklined apparatus that is divided into two separate chambers for electrolysis and metal collection, respectively (Figure 20.9). Densely packed, cooled graphite anode plates (b) are installed through the roof and double-acting steel plate cathodes (c) through the back wall. Chlorine (98%) is collected from a central pipe in the anode compartment. Circulation of the electrolyte (h) is parallel to the electrodes bringing the magnesium metal to the collecting chamber from where it is extracted by vacuum and transported to the foundry. This cell operates on solid or liquid cell feed conveyed continuously or at intervals to the cell at $700\text{--}720^\circ\text{C}$ with a current load of 350–400 kA. Energy consumption is 12–14 kWh per kilogram of magnesium and cell life exceeds five years.

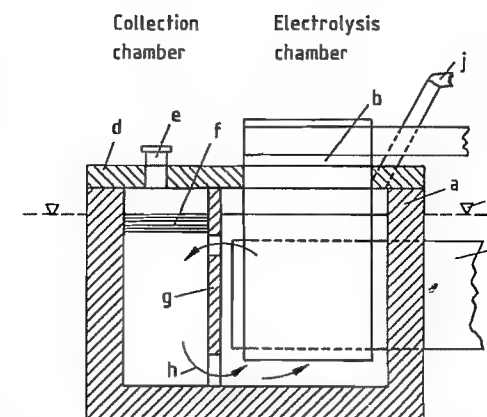


Figure 20.9: Norsk Hydro cell: a) Refractory material; b) Graphite anode; c) Steel cathode; d) Refractory cover; e) Metal outlet; f) Metal; g) Partition wall; h) Electrolyte flow; i) Electrolyte level; j) Chlorine outlet.

VAMI Cell. The cell developed by VAMI, St. Petersburg, is based on the same principles as the Norsk Hydro cell but operates at $150\text{--}180^\circ\text{C}$ and 700–740 °C. Various electrode arrangements are reported. Current density varies between 1000 and 5000 A/m², with a preferred optimum at 2000 A/m². The low-carbon steel used for the cathodes is claimed to undergo transformation during operation from 0.2–0.3% carbon to 0.02% carbon, thus coarsening the ferritic grains 100-fold and improving current efficiency. When operated on dehydrated molten magnesium chloride obtained after reduction of titanium(IV) chloride with magnesium (Kroll process), the current efficiency is ca. 0.80, with an electric energy consumption of 13.5 kWh per kilogram of magnesium [22].

Alcan Cell. Magnesium cells developed by Alcan, Canada, for the electrolysis of anhydrous magnesium chloride have been operating since 1961 in Japan and the United States. They are used in titanium plants where magnesium is employed in the reduction of titanium(IV) chloride (Kroll process). The cells are divided by a curtain wall into a front compartment where the metal accumulates on the heavier chloride bath and an electrolysis compartment where chlorine ($\geq 97\%$) is collected.

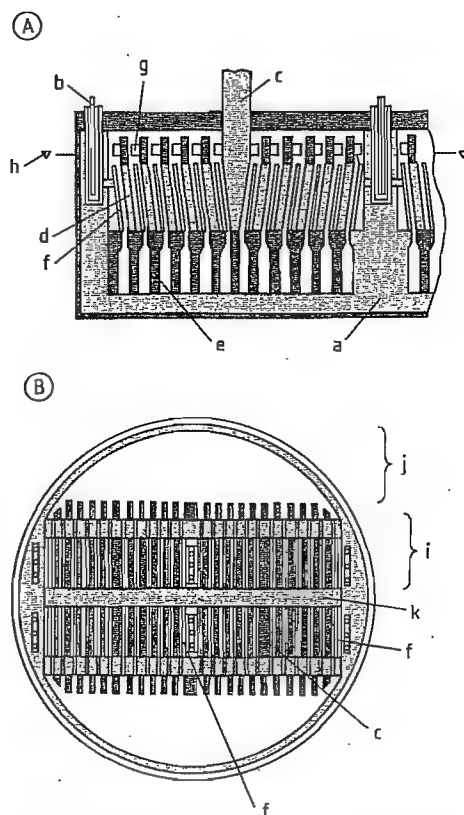


Figure 20.10: Vertical section (A) and top view (B) of Ishizuka cell: a) Refractory material; b) Steel cathode; c) Graphite anode; d) Bipolar electrode (steel-graphite); e) Bipolar support; f) End cathode; g) Electrolyte ports; h) Electrolyte level; i) Electrolysis chamber; j) Metal-collecting chamber; k) Refractory wall.

The two compartments have insulating covers through which water-cooled graphite anodes are installed. The cathodes are parallel to the anodes and are installed through the refractory back wall below the bath level. The operating temperature (660–680 °C) is controlled just above the melting point of the metal.

A new multipolar cell design has been in operation since 1982 in which electrodes are added between the anode and the cathode surfaces. The energy consumption of this cell when operating on high-purity molten magnesium chloride from Kroll titanium production is claimed to be 9.5–10 kWh per kilogram of magnesium. Cell productivity has reached

1000 t/a. The cell operates at 100 kA with a life of up to two years [28].

Ishizuka Cell. The Ishizuka Research Institute, Japan, has developed a bipolar cell that has been used since 1983 for industrial magnesium production by Showa Titanium, Toyama (Figure 20.10).

The outer, brick-lined, cylindrical, water- or air-cooled shell is divided in half by a refractory wall (k). Each half is subdivided with a refractory partition wall into a metal-collecting chamber (j) and an electrode chamber (i) where electrolysis is performed. The electrode chambers have three steel cathodes, one at each end and one in the center (b); a graphite anode (c) is located between each pair of cathodes. Five bipolar electrodes (d) are located between each set of anodes and cathodes. The bipolar electrodes are made of graphite with steel plates attached to the cathode side. The current load is connected to the cathodes and graphite anodes penetrating through the refractory-lined cover of the cell. The bipolar electrodes are submerged in the electrolyte. The electrolyte flow induced by gas production carries the metal into the collecting chamber through openings in the partition wall. The electrolyte returns to the electrode chamber in the bottom part of the cell. The cell operates at 670 °C and carries 50 kA, corresponding to 300 kA in a monopolar cell. Current density is 5600 A/m², and the interpolar gap is 4 cm. At a current efficiency of 0.76, the power consumption is 11 kWh per kilogram of magnesium when operated on molten magnesium chloride from Kroll titanium production. The furnace cell life is ca. three years.

The prime advantage of the bipolar cells is reduction of heat losses. Special provisions are made to prevent current leaks from bypassing the bipolar electrode system. Ishizuka states a preferred electrolyte composition of 50% NaCl, 30% KCl, and 20% MgCl₂. The cell maintained at a pressure of 0–1.33 kPa yields ≥ 96% chlorine [29].

Dow Cell. Electrolysis of hydrous cell feed (MgCl₂·1.5H₂O) in the Dow cell (Figure 20.11) requires graphite anodes which can be

lowered into the cells to compensate for consumed graphite. Densely packed cylindrical anodes (c) are led through openings in the refractory cell hood (d) and sealed to reduce air leaks. They are centered by insulating ceramic spacers. The development of efficient anode seals to withstand severe corrosive environment and high temperature has been a challenge. Conical cathodes (b) are welded to the steel shell (a) holding the electrolyte. Magnesium metal is conducted by The electrolyte flow to a collecting chamber (e) at the front of the cell. Water in the cell feed is partly flashed off, and partly reacts with chlorine (to form HCl) and with oxygen in the graphite (to form CO and CO₂). Graphite consumption is probably 60–70 kg per tonne of magnesium. The Dow cell is operated at 700 °C with an estimated current load of 180 kA and current efficiency of ca. 0.8.

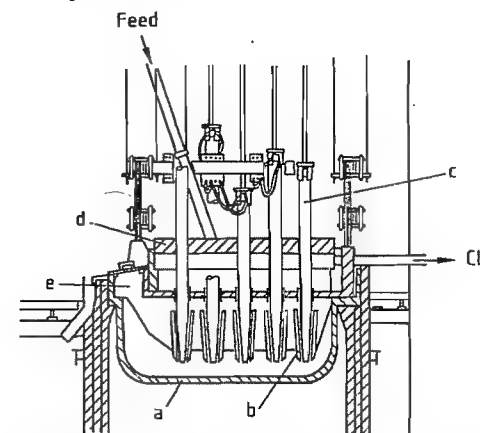


Figure 20.11: Dow cell: a) Steel mantle; b) Steel cathode; c) Graphite anode; d) Refractory cover; e) Magnesium collection compartment.

In comparison with an anhydrous cell feed, the hydrous cell feed increases electric power consumption as well as the formation of sludge and dilute anode gases. The presence of hydrogen, chlorine, and carbon in the cell at high temperature promotes formation of chlorinated hydrocarbons in off-gases.

Dow has patented an inert anode that is protected by a ceramic cover of doped and sintered Ti⁴⁺ and Ti³⁺ compounds [30], which could improve the performance of the cell. Ef-

forts to reduce the overall energy consumption in Dow's operations from 325 MJ per kilogram of magnesium in 1978 by 15–20% over ten years have been reported [8, 21].

20.5.2 Metallothermic Reduction

Industrial metallothermic processes for magnesium production are based on the reduction of magnesium oxide with ferrosilicon (FeSi). Magnesium oxide is provided in the form of calcined dolomite (MgO·CaO), sometimes enriched with calcined magnesite (MgO). The basic reaction is:



This reaction is highly endothermic ($\Delta G \approx 210$ kJ/mol). The vapor pressure at 1800 °C is 0.1 MPa. Industrial processes operate under vacuum at a lower temperature (1200–1500 °C) to limit wear on construction materials and to suppress undesirable side reactions in the gas systems. Reduction is carried out in the batch mode. Various reactor designs have been suggested [31]; determining factors are transfer of heat to the charge and attempts to develop a continuous process. Active developmental work aims at increasing reactor capacity and improving metal yield [32].

Three principles are applied for the reaction chamber:

- Externally heated retorts producing 70 kg/d (Pidgeon)
- Internally heated reactors producing 2 t/d (Bolzano)
- Internally heated reactors with molten slag producing ca. 12 t/d (Magnetherm)

Pidgeon Process. The process developed by PIDGEON in the early 1940s is presently used by Timminco in Canada and Ube Industries in Japan (Figure 20.12). Briquettes of crushed calcined dolomite and ferrosilicon fines in a stoichiometric ratio of 2:1 are loaded into tubular refractory steel retorts, heated externally to a reaction temperature of 1200 °C, and evacuated to 13.3 Pa. Magnesium vapor condenses at the cooled end of the retorts.

Reaction kinetics depend on the thermal conductivity of the briquettes, the shrinking

core pattern of the reaction zone, and the diffusion rate of magnesium vapor. Heat transfer to the charge limits the diameter of the retorts. Timminco operates retorts that are 3 m long and have a bore diameter of 275 mm, each retort yields 70 kg of magnesium per day. Ferrosilicon grades containing 65–90%, but preferably 75–90% silicon, have been used. Metal recoveries up to 90% are attainable if a slight excess of silicon above stoichiometric requirements is used. Recovery increases with increasing ferrosilicon concentrations. Handling of the charge and removal of slag and condensate have been highly automated reducing down time to 1 h per day. The productivity of the Pidgeon process is now 25 t/a per employee with a total energy requirement of 30 kWh/kg. The high-purity dolomite from Haley (99.5% $\text{CaCO}_3 \cdot \text{MgCO}_3$) enables Timminco to produce 99.95%, and even 99.98%, magnesium in commercial quantities. The company has recently introduced to the market ultrapure AZ 91 alloys with improved corrosion resistance [33].

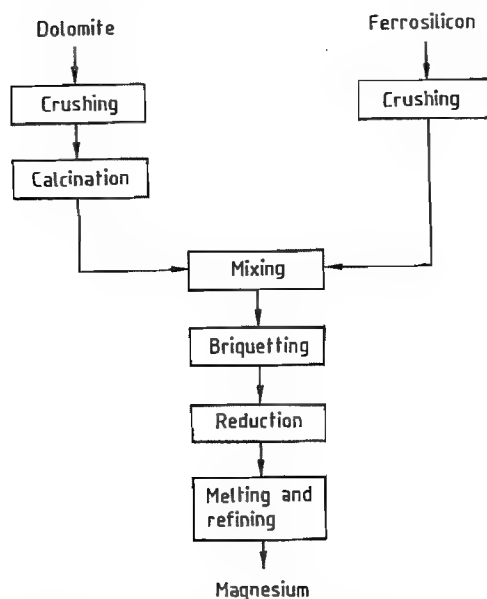


Figure 20.12: Flow sheet for the production of metallurgical magnesium (Pidgeon and Bolzano processes).

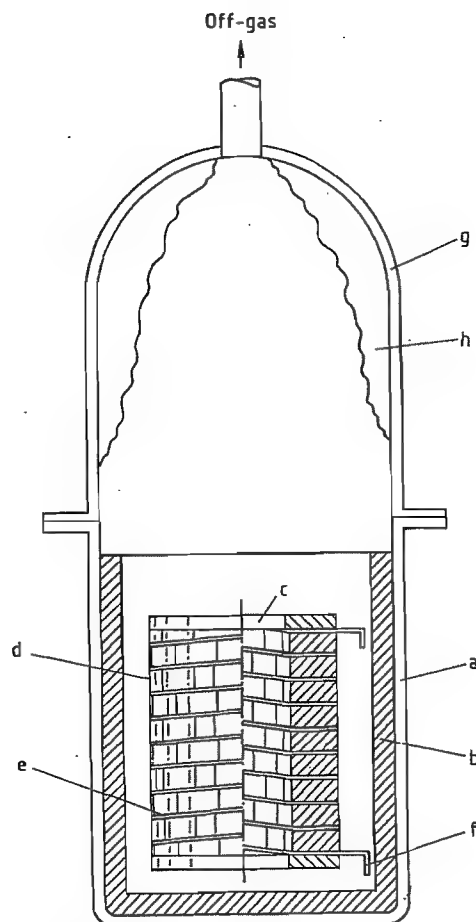
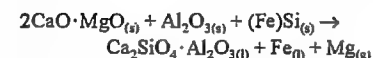


Figure 20.13: Bolzano reactor: a) Steel mantle; b) Refractory; c) Removable charge pack; d) Charge briquettes; e) Charge support; f) Electric heating connection; g) Removable condenser; h) Condensed magnesium.

Bolzano Process. The Bolzano process is operated in Italy by Società Italiana per il Leghe di Magnesio (SAIM) and in Brazil by Brasmag. It employs an internally heated, brick-lined cylindrical reactor (Figure 20.13). The briquetted charge of homogeneously mixed calcined dolomite and ferrosilicon lines (d) is loaded on a charge support system (e). Internal electrical heating (f) is conducted to the charge through the charge support system. The process operates at 1200 °C and < 400 Pa. Magnesium vapor condenses inside the condensers that are water-cooled to 400–500 °C. Each re-

actor has a production capacity of ca. 2 t of magnesium per 20–24 h reaction cycle, with a shutdown time of 0.5–0.75 h per cycle. Production of 1 t of magnesium consumes 7–7.3 MWh, 5–5.2 t calcined dolomite, and 0.7 t of silicon contained in 78% ferrosilicon, with 81% silicon recovery; 5–5.2 t of slag is produced per tonne of magnesium and sold for use in plaster and building bricks. Mechanization of charge handling and slag removal is a challenge in this process. Magnesium with a purity of 99.98–99.99% is obtained [34].

Magnetherm Process. The magnetherm process was developed by Pechiney Électrometallurgie in 1963 and is still in use at the company's magnesium extraction plant in Marignac, France. The process is now also operated by North West Alloys (United States), Japan Metals and Chemicals (Japan), and Magnohrom (former Yugoslavia). The total installed production capacity worldwide is 65 000 t/a. The overall equation for the process is



The dicalcium silicate slag formed in the reaction of calcined dolomite with ferrosilicon (Pidgeon and Bolzano processes) has a melting point of 2000 °C and is solid at the reaction temperature (1200 °C). The Magnetherm process, however, operates with a partly molten slag of the general composition $2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{Al}_2\text{O}_3$ at 1550–1600 °C. The slag contains 50% Ca_2SiO_4 , 18% Al_2O_3 , 14% MgO , and 18% CaO and is kept in an electrically heated, cylindrical, brick- and carbon-lined steel vessel (Figure 20.14). The power input (4500 kW) is conveyed through a water-cooled copper electrode (a) from the top through the slag (g) to the bottom graphite lining (b) of the reactor, which acts as a power outlet. Coarse calcined dolomite and alumina screened to 3–30 mm, as well as ferrosilicon containing a minimum amount of fines, are added continuously to the slag under a vacuum of 0.40–0.67 kPa through charge holes in the water-cooled furnace roof. Magnesium vapor condenses in a separate condenser system.

The main impurities of the metal produced at Marignac (France) are manganese 0.04%, silicon 0.03%, iron 0.01%, zinc 0.007%, and copper 0.005%.

The slag is not homogeneous and contains about 40% solid Ca_2SiO_4 . The main endothermic reaction takes place close to the surface of the slag. Deeper in the molten slag, the higher pressure slows down and finally stops the reaction at a ferrosilicon content in the bottom layer of ca. 20%. Slag and 20% ferrosilicon are tapped twice during a cycle of ca. 18 h, having produced more than 10 t of magnesium. Adjustment of the slag composition to higher magnesium oxide content and heating the surface of the slag with arc or plasma burners to 1900–1950 °C have been suggested to allow reduction to occur at atmospheric pressure [35].

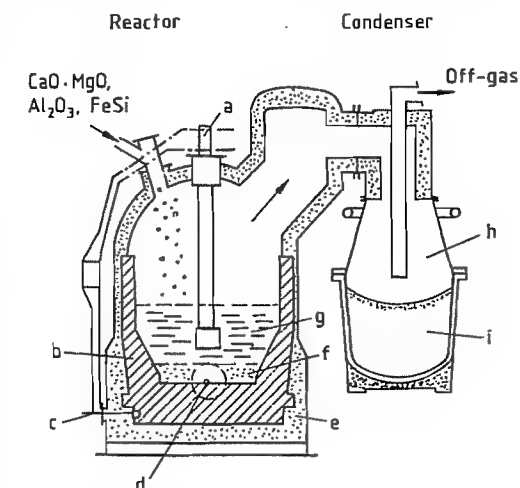


Figure 20.14: Magnetherm reactor: a) Copper electrode; b) Graphite lining; c) Bottom electrode; d) Taphole; e) Refractory; f) Low-grade FeSi; g) Slag; h) Condenser; i) Condenser crucible.

Production of 1 t of magnesium requires 5.7 t calcined dolomite, 0.75 t bauxite, 0.65 t of silicon contained in 77% ferrosilicon (88% Si recovery), and < 9 MWh of power. About 6 t of slag is produced per tonne of magnesium and is used in the cement industry for road building and as a source of magnesium and silicon in agricultural soil. The 20% ferrosilicon by-product (yield 0.15 t per tonne of magne-

sium) is used in the metallurgical industry, in the production of heavy liquid media for the separation of metals, or in drilling mud. The productivity of the process is estimated to be ca. 50 t per manyear [36].

20.5.3 Refining and Casting

All magnesium extraction processes are followed by refining to remove impurities and casting to convert the metal to ingots, billets, slabs, or granules [5].

Refining. Nonmetallic impurities in the form of particulate oxides, nitrides, carbides, and chloride inclusions impair corrosion resistance as well as mechanical and surface properties. Most alkali chloride and magnesium chloride fluxes wet and coat the surface of the impurity particles. The higher density of the chlorides causes the impurities to sink to the bottom of the melt as a sludge. Fluxes are composed to maintain a minimum difference in density compared to that of the metal of 0.15–0.20 g/cm³.

Inspissating (thickening) agents such as magnesium oxide and calcium fluoride reduce the fluidity of the sludge to prevent it from contaminating the metal after settling. Inspissated fluxes are also used to protect the metal surface during holding and casting because of their viscosity and stability (Table 20.5).

Table 20.5: Composition of fluxes used in melting and refining (%).

Purpose	CaCl ₂	NaCl	KCl	MgCl ₂	CaF ₂	MgO
Melting	40	30	20	10		
Melting and refining	20	10	10	35	15	10
Refining	15	10	10	35	20	10

Metallic impurities are normally controlled by the choice of raw materials and extraction process parameters. The most common metal impurities in pure magnesium are iron, copper, nickel, manganese, zinc, aluminum, silicon, calcium, and sodium. Intermetallic particles of aluminum, manganese, iron, and silicon have also been identified.

Heavy metals reduce the corrosion resistance of magnesium while acting as cathodes

in galvanic cells in the metal. Metallic impurities are also undesirable for certain applications in which magnesium is used as a reductant (Ti, Zr, U) or as a canning material for the fuel elements in nuclear reactors where the metal's neutron absorption properties are important.

The solubility of iron in magnesium increases with temperature (Figure 20.15). Iron levels can be kept low by operating at low temperature (660–680 °C) under clean conditions [37]. The iron content can be reduced further by adding manganese, zinc, beryllium, or titanium(IV) chloride. Silicon can be removed by adding zinc chloride or cobalt(II) chloride. In these processes, complex iron and silicon compounds precipitate. Sodium and calcium are efficiently reduced and converted to their chlorides by stirring magnesium chloride into the melt [5].

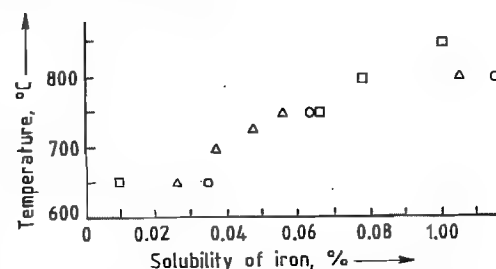


Figure 20.15: Solubility of iron in magnesium [36]. Symbols indicate results obtained from different sources.

Hydrogen is formed when magnesium reacts with moisture contained in the air or in materials used in the process. The normal level of hydrogen in pure magnesium is 1–7 cm³ per 100 g, which is acceptable for most purposes. Higher levels cause porosity on solidification; this is especially important in magnesium alloys. The level of dissolved hydrogen can be reduced by treatment with chlorine at 725–750 °C, nitrogen at 650–680 °C, argon, or helium.

Equipment. The standard equipment in magnesium refineries consists of large, stationary, brick-lined furnaces or externally heated steel crucibles containing 10–25 t or 2–6 t of molten magnesium, respectively. The stationary furnaces can be heated electrically,

with gas or oil burners from the roof, or by submerged electrical heating systems.

Electrolytic magnesium recovered and processed in the molten state can be refined in continuous stationary furnaces. Proprietary installations are in use with metal yield > 99.5% and negligible flux consumption (Figure 20.16) [38].

Metallothermic magnesium crowns (condensed magnesium crystals) or condensates are recovered in the solid state. Standard practice involves batchwise melting and refining in steel crucibles that are transported by crane to the casting area. The melting process and the high content of nonmetallic impurities require a flux consumption that is 5–10% of the metal volume; metal recoveries are in the range 95–98%.

Casting. Highly automated casting by pumping or static pressure is state of the art. Magnesium contracting 4.2% during solidification and 5% during cooling to 20 °C is sensitive to surface cracks and shrink holes. Turbulent flow favors the formation of nonmetallic inclusions. Consequently, care is taken to control the solidification process and to reduce turbulence. At elevated temperature or in the case of turbulent metal flow, sulfur dust may be sprayed on the metal surface to suppress oxidation.

The level of impurities in standard 99.8% magnesium does not influence the solidification pattern. Pure magnesium solidifies at its

melting point (649 °C). During holding and casting, the metal surface is protected against oxidation by a cushion of protective gas. Air may be completely replaced by helium or argon; low concentrations of sulfur hexafluoride or sulfur dioxide in air form protective layers on the metal surface. Blends of air, sulfur hexafluoride, and carbon dioxide are being used increasingly because of their nontoxic character and low cost [39].

Billets are cast in multistrand continuous or semicontinuous direct-chill casting machines. The number of parallel strands is limited to four to six because of practical problems associated with the metal's low heat content and tendency to skin formation. Hot top and airslip systems are state of the art.

Single-crystal magnesium may be continuously cast by the Ohno horizontal continuous casting process. The metal is cooled directly with a water spray immediately outside the mold maintained at a temperature above the melting point (64 °C). The rapid cooling produces metal with unidirectional solid structure, which is reported to exhibit excellent workability and superior anticorrosion properties [40].

To avoid discoloration and surface corrosion during transportation and handling under severe climatic conditions, the metal is protected by suitable ventilated plastic or paper wrappings. Magnesium ingots are sometimes protected by a thin layer of mineral oil.

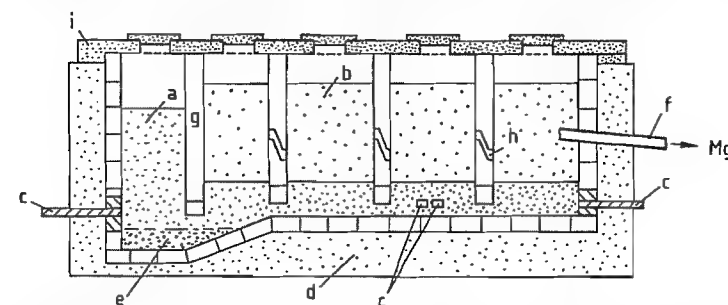


Figure 20.16: Norsk Hydro refining furnace [38]: a) Salt melt; b) Magnesium metal; c) Electrodes; d) Refractory; e) Sludge; f) Tapping spout; g) Partition wall; h) Metal port; i) Refractory cover.

20.5.4 Particulate Magnesium

Particulate magnesium comprises powders, granules, turnings, and raspings; particle sizes range from 0.04 to 5 mm, and particle shapes vary. Particulate products are used in chemical and metallurgical processes in which magnesium acts as a reagent, catalyst, or alloying element. Fine powders are used in pyrotechnics.

Particulate magnesium is considered inflammable and subject to specific labeling and packing regulations according to IMDG codes classes 4.1 and 4.3; UN No. 1869 and 1418; CFR 49: 172.01, flammable solid; RID/ADR class 4.1, number 13b, class 4.3 number 1d.

Flowability, uniformity of grain size, and defined area volume ratios are important for injection into molten metal (steel, aluminum). Particulate magnesium is frequently blended with inert and active components (e.g., lime or alumina) or coated with salt or refractories. These products are used for desulfurization of iron. Blending and coating reduce the reactivity and increase the magnesium yield. Turnings and raspings commonly used for Grignard syntheses and pharmaceuticals are adjusted for reactivity (surface-to-weight ratio) and form of the particles according to customer specifications. Finely divided powder for pyrotechnics is subject to narrow tolerance limits, including the content of organic material.

Particulate magnesium is produced directly from the molten state by shotting, atomization, or granulation or by machining ingots, slabs, or billets, with subsequent grinding and screening. Airborne dust with a particle size < 0.15 mm is explosive. Safety precautions for machining and atomizing operations include prevention of explosion hazards in the processing and handling of fine dust, as well as design of the general plant layout to limit the consequences of accidental blowouts. Clean operation and personal hygiene are important.

Nearly spherical magnesium shots in the 0.2–2-mm size range are produced by nozzle spraying in a cooling tower with an inert atmosphere [41]. Atomizing is performed in a pro-

TECTIVE atmosphere of argon, helium, or methane. Magnesium may be atomized on a rotating disk or in a gas stream. During shotting and atomizing, precautions are taken to avoid the formation of layers of highly ignitable, pyrophoric substances.

Salt-coated granules were originally developed in the former Soviet Union and are produced by mixing alkali chloride salts and molten magnesium in a rotating perforated cup; the metal is disintegrated by centrifugal force with subsequent air cooling. Spheroidal particle sizes range from 0.2 to 2.5 mm, with a salt content of 10% [22, 42]. Other methods include mixing molten mixtures of magnesium and alkali chlorides and adding a stabilizing boron compound [43]. Various proprietary processes employ eutectic salt compounds with low hygroscopicity to produce particles with high flowability [44]. The salt and metal are separated by gentle crushing and screening, leaving granules with 5–10% salt as coating. The production of salt-coated granules is safer than that of pure magnesium powder and can be integrated in normal foundry operations.

20.6 Environmental Aspects

All magnesium extraction processes require installations for cleaning off-gases and treating wastewater. Significant amounts of solid waste are deposited as landfill. All processes involve calcination of carbonaceous minerals or dehydration of hydroxides in which dust is removed by conventional methods. Gases emitted to the atmosphere contain carbon dioxide, nitrogen oxides, and sulfur dioxide from the combustion and calcination processes. The content is frequently lowered by scrubbing the gases with seawater to comply with local emission regulations.

In *electrolytic processes*, carbon is used as a reductant in the preparation of anhydrous magnesium chloride and as anode material in electrolysis. The presence of carbon, water, chloride, or hydrogen chloride, even in low concentrations, at elevated temperature leads

to formation of chlorinated hydrocarbons and other organic compounds. Chloromethanes, chlorobenzenes, polychlorinated biphenyls, chlorodibenzofurans, and chlorodibenzo-*p*-dioxins are highly toxic and are only slowly degraded in nature. Although such compounds only occur in liquid effluents from scrubber systems at low concentrations (a few micrograms per liter), collection and destruction are mandatory.

Chlorinated organic compounds can be either in solution or present as small particles in the liquid effluents. Particles may be flocculated with appropriate cationic or nonionic agents. The agglomerates adhere to solid inorganic particles that are often present in the effluents (carbon and hydroxides or oxides of iron, aluminum, silicon, etc.). The particles are removed by filtration or centrifugation. Liquids may be treated with activated carbon. Traces of chlorine or hydrochloric acid in off-gases are scrubbed, recycled, or neutralized by conventional methods.

By-products from *metallothermic processes* are either used for industrial purposes or deposited as landfill.

Sludge from *foundry operations* contains entrapped metallic magnesium globules. When deposited as landfill, precautions must be taken to control hydrogen emission from the reaction of entrapped magnesium with water. Off-gases from foundry operations containing hydrogen chloride, sulfur dioxide, and magnesium oxide are scrubbed by conventional methods to comply with local regulations.

20.7 Quality Specifications

The ASTM designation B 92M-83 covers pure magnesium in the form of ingot or stick for remelting in the following grades: 9980, 9990, 9995, and 9998 (Table 20.6). Examples of other standards for pure magnesium corresponding to those of the ASTM are ISO 8287 and DTN 17800.

Table 20.6: Magnesium grades according to ASTM B 92M-83. Figures refer to maximum content in weight percent except otherwise specified.

Component	9980 A	9980 B	9990 A	9995 A	9998 A
Aluminum			0.003	0.01	0.005
Copper	0.02	0.02			0.0005
Iron			0.04	0.003	0.002
Lead	0.01	0.01			0.001
Manganese	0.10	0.10	0.004	0.004	0.002
Nickel	0.001	0.005	0.001	0.001	0.0005
Silicon			0.005	0.005	0.003
Tin	0.01	0.01			
Titanium				0.01	0.001
Other impurities (each) ^a	0.05	0.05	0.01 ^b	0.005 ^b	0.005 ^b
Magnesium (by difference, min.)	99.80	99.80	99.90	99.95	99.98

^a For specific applications, other minor impurities may be limited by agreement.

^b For nuclear applications, cadmium and boron concentrations are specified as follows: Cd (min. 0.00005; max. 0.0001%); B (min. 0.00003; max. 0.00007%).

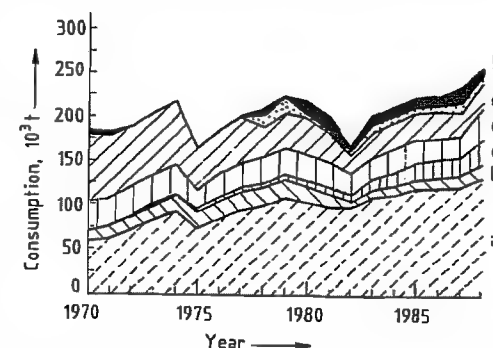


Figure 20.17: Consumption by end uses. Pure magnesium: a) Aluminum alloys; b) Iron nodularization; c) Desulfurization; d) Chemical applications. Magnesium alloys: e) Pressurized die casting; f) Structural applications. Pure magnesium and alloys: g) Other uses.

Grade 9980A is adequate for most uses and can be obtained by electrolysis by using controlled standard operations. Grades 9995A and 9998A are normally produced only by metallothermic processes. High-purity magnesium can also be produced by distillation of lower grades, but this is expensive [5, p. 178; 22, p. 313].

20.8 Uses

The uses and consumption of magnesium are summarized in Figure 20.17. The overall growth rate in the use of magnesium is esti-

mated as of 1989 to be 3–4% for the next few years.

Aluminum Alloys. The largest single use of magnesium is as an alloying element in aluminum alloys. Aluminum–magnesium alloys have improved ductility, enhanced resistance to saltwater corrosion, and improved cryogenic properties. User forms are ingots weighing 1–25 kg or sows weighing 250–500 kg. The market growth of this application depends on the growth of aluminum and the recycling efficiency of aluminum scrap, particularly beverage cans.

Desulfurization and Nodularization. In the iron and steel industry magnesium is used for desulfurization and nodularization. Particulate magnesium alone or blended with other ingredients is injected into crude iron melts. The typical magnesium consumption for desulfurization of low-iron steel is 0.5 kg per tonne of steel. Magnesium also triggers the transformation of laminar carbon to globules in nodular iron. For this purpose the metal is either added with ferrosilicon as an alloying element or directly in the form of lumps, impregnated coke, or granules. Magnesium has a modifying effect on nonmetallic inclusions in steel. Effect and user forms are currently being studied [45].

Magnesium-based alloys are normally delivered as alloyed ingots from the primary producers. Magnesium alloys are used for pressure die casting, structural applications, numerous lightweight applications (automotive, hand tools, computers, etc.), and where the metal's damping capacity is of importance. The magnesium-based magnox alloys are used in extruded form as canning materials in gas-cooled nuclear reactors (Calder Hall) because of their low neutron absorption area. Uses of magnesium for uranium and nuclear application account for less than 1% of the market in the Western world [46].

Chemical applications include the use of magnesium as a reagent in the production of titanium and zirconium by the Kroll process, the reduction of uranium fluoride to uranium

metal, and the production of beryllium and hafnium. Titanium constitutes by far the largest user segment in this group, the magnesium being added in ingot form. Magnesium chloride from the Kroll process is electrolyzed to recover magnesium and chlorine. The normal magnesium requirement to compensate for losses is 0.1 t per tonne of titanium.

Magnesium raspings for the production of metallic uranium have a specified limited content of boron, cadmium, and rare-earth elements including gadolinium, samarium, europium, and dysprosium.

The use of particulate magnesium, raspings, or turnings in Grignard syntheses has been declining, due primarily to restricted use of tetraethyllead.

Other Uses. The electronegative character of magnesium is used for corrosion abatement as sacrificial soil and hot-water tank anodes. European restrictions on aluminum in drinking water have encouraged the use of magnesium anodes for hot-water tanks. Magnesium batteries for military purposes and rescue systems combine light weight and high energy content.

Pure magnesium (preferably atomized powder) combines readily with hydrogen to form magnesium hydride which can be released in a reversible process. Magnesium hydride has a higher concentration of hydrogen per unit volume than liquid hydrogen. The reversibility of the process is dependent on the surface activity of the powder. Magnesium as a carrier for hydrogen could represent a future use [47].

20.9 Economic Aspects

Considered a strategic material for military applications during and shortly after World War II, magnesium is now used predominantly for nonmilitary purposes. Since the oil crises in the early 1970s, magnesium consumption has fluctuated in line with other commodity materials dependent on changes in the industrial growth in major consumer countries. The capacities are given in Table 20.7.

Table 20.7: Main magnesium producers.

Company	Installed production capacity, 10 ³ t	Production process
Norsk Hydro a.s., Norway	1	electrolytic
Norsk Hydro Canada, Canada	(40)	electrolytic ^a
Dow Chemical, USA	90	electrolytic
Amox, USA	35	electrolytic
Northwest Alloys, USA	35	thermic
Pechiney Électrometallurgie, France	15	thermic
MagCan, Canada	(12)	electrolytic ^b
Timminco, Canada	12	thermic
Magnesio (SALM), Italy	10	thermic
Ube Industries, Japan	7	thermic
Furukawa Magnesium Co., Japan	(6)	thermic ^c
Brasmag, Brazil	5	thermic
Magnohrom, Yugoslavia	5	thermic
Japan Metals and Chemical Co., Japan	3	thermic
Former Soviet Union	86	electrolytic
China	9	electrolytic

^a Capacity under installation; start-up planned mid-1989.

^b Capacity under installation; start-up planned early 1990.

^c Facility closed in 1988.

Total production of magnesium in the Western world in 1988 was 241×10^3 t, and consumption was 255×10^3 t, including 13.2×10^3 t exported to Eastern countries. Approximately 75% of the total world magnesium production (1989) is electrolytic and 25% metallothermic. The main Western consumer regions were North America (125×10^3 t) Latin America (11.7×10^3 t), Europe (73.3×10^3 t), Africa and the Middle East (3.8×10^3 t), and Asia-Oceania (37.2×10^3 t) (source: International Magnesium Association). The per capita consumption was 0.51 kg in the United States, 0.18 kg in Japan, 0.17 kg in Western Europe, and 0.04 kg in South America.

World production of primary magnesium in the five-year periods 1963–1967 and 1983–1987 is summarized in Table 20.8. Growth in the interval between these periods occurred primarily in Norway, the former Soviet Union, and the United States. In 1983–1987 the United States was the largest producer (ca. 40% of the world total), followed by the former Soviet Union (28%) and Norway (15%). Significant growth is anticipated in Canada, with an additional capacity of more

than 50 000 t annually expected to come on stream in 1989.

The per capita consumption of magnesium in selected countries is summarized in Table 20.9. In 1983–1987 the United States had the highest consumption, followed by the Soviet Union and Japan.

The metal is not traded on the London Metal Exchange, and the major producers control their own distribution network. Price fluctuations have been less cyclical than for other metals in world trade (Figure 20.18).

Table 20.8: Average annual world primary magnesium production (10³ t), as reported by the U.S. Bureau of Mines, Department of the Interior.

Country	1963–1967	1983–1987
Brazil		3.4
Canada	8.0	7.0
China	0.9	7.0
France	2.6	13.2
Italy	6.2	9.3
Japan	4.2	7.6
Norway	24.7	48.2
Former Soviet Union	34.7	87.0
United Kingdom	4.7	
United States	7.5	127.2
Yugoslavia		4.5
World total	161.3	314.4

Table 20.9: Average annual per capita primary magnesium consumption (kg) in selected countries.

Country	1963–1967	1983–1987
Australia	0.054	0.255
Brazil	0.233	0.417
Canada	0.220	0.243
China	0.001	0.012
France	0.085	0.175
West Germany	0.632	0.458
Italy	0.025	0.076
Japan	0.050	1.633
Norway	0.270	0.967
Soviet Union	1.243	2.629
Sweden	0.069	0.188
Switzerland	0.119	0.298
United Kingdom ^a	0.164	0.084
United States	3.258	2.986

^a Includes secondary magnesium.

Magnesium duty tariffs are regulated by the General Agreement on Tariff and Trade (GATT). In 1989 the following export tariffs were applied on pure magnesium: to the United States from Europe 8%, Canada 7.2%, and Brazil 0%; to Canada from the United

States 3.6% (declining to 2.8% by 1991) and Europe 4%; and to Europe from the United States, Canada, and Brazil 5.3%.

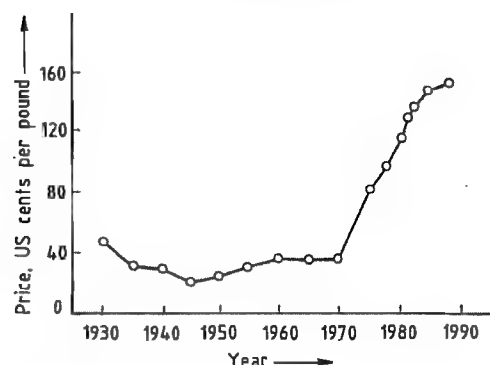


Figure 20.18: Magnesium prices.

20.10 Toxicity and Occupational Health

Magnesium and magnesium compounds are regarded as having low toxicity. No reports of serious poisoning in industry have appeared in the literature. Industrial exposure of humans resulting in magnesium serum values twice the normal level did not cause any ill effects [48]. In humans the only sign of acute toxicity is metal fume fever resulting from inhalation of freshly generated magnesium oxide. This is in contrast to animals, where magnesium cause both systemic and cutaneous responses. No evidence is available that inhalation of magnesium dust can cause lung injury. However, fine magnesium dust is generated in the printing trade, and complaints have been made about discolored sputum [49].

The acute oral toxicity of magnesium compounds in animals is low: LD₅₀ values (rat, oral) for magnesium nitrate and chloride are 5440 and 2800 mg/kg, respectively. However, oral intake can impair kidney function; toxic symptoms include a sudden drop in blood pressure and respiratory paralysis due to depression of the central nervous system (CNS) [48]. Intravenously administered magnesium compounds have been shown to be more toxic to animals than orally administered com-

pounds. Toxic response includes general anesthesia and narcosis. Intravenous administration of calcium counteracts the reaction.

Magnesium is essential for metabolic reactions involving ATP. It is a cofactor for enzymes that participate in transfer of phosphate from ATP and other nucleotide triphosphates. However, the activity of a large number of enzymes is also magnesium dependent (e.g., phosphatases and pyrophosphatases).

Some effects of magnesium on the nervous system are similar to those of calcium. An increased concentration of magnesium in the extracellular fluid causes CNS depression. Hypomagnesemia causes increased CNS irritability, disorientation, and convulsions.

In the cardiovascular system some of the effects of excess magnesium are similar to those of potassium. Magnesium has a direct depressant effect on skeletal muscle.

Magnesium salts are poorly absorbed from the alimentary tract, and primarily from the small intestine. Net magnesium absorption is 35–40% with a normal dietary intake and increases to ca. 80% at low magnesium intake. Nutritional requirements have been calculated to be approximately 150 mg/d for maintaining a normal plasma level [50]. Normal adult dietary intake is 300–400 mg/d. Drastic reduction of dietary intake of magnesium is needed to induce a negative balance because of extremely effective renal retention and increasing intestinal absorption. The effect of magnesium (as well as of zinc) supplementation and depletion on carcinogenesis has been reviewed comprehensively [51]. Magnesium (or zinc) supplementation tends to inhibit carcinogenesis, and magnesium deficiency increases the incidence of neoplasia in humans and animals.

Various magnesium compounds such as magnesium hydroxide (milk of magnesia) are used as gastric antacids and can also be components of poison antidotes. Magnesium sulfate acts as a purgative because it is poorly absorbed from the gut and causes osmotic withdrawal of water from the gut wall. Fatal intoxication can occur with very high dietary

levels (15 000–25 000 ppm) or under circumstances that increase magnesium absorption [52].

Particles of metallic magnesium that perforate the skin or gain entry through cuts and scratches may produce a severe local lesion characterized by evolution of gas and an acute inflammatory reaction, frequently with necrosis (chemical gas gangrene). Gaseous blebs may develop within 24 h of injury and are very slow to heal. However, the most serious hazard presented by magnesium is the danger of burns from molten metal.

20.11 Compounds

Magnesium occurs in divalent form in all of its compounds. The bromide, iodide, sulfate, and nitrate salts are water soluble. Some of the water-soluble salts are highly hygroscopic and form crystals with a high water content. Magnesium fluoride, oxide, hydroxide, phosphate, and carbonate are sparingly soluble or insoluble in water.

The water-soluble magnesium salts tend to undergo hydrolysis and form basic salts due to the weakly basic character of magnesium hydroxide. This is responsible for the highly corrosive action of magnesium salt solutions; dehydration of magnesium salts containing water of crystallization without hydrolytic decomposition is also difficult to achieve.

The most important magnesium compounds are magnesium oxide, which is used for refractory magnesia bricks and as a heat-storage medium, and magnesium chloride which is electrolyzed to produce magnesium metal. Naturally occurring magnesium carbonate (magnesite) is mainly burned to give sintered magnesia for the production of magnesia bricks. Seawater is an important source of magnesium oxide and magnesium chloride. Calcined dolomite (CaCO₃·MgCO₃) is used as a raw material for the silicothermic production of magnesium metal. Basic magnesium carbonate is used for thermal insulation.

Anhydrous magnesium nitrate is difficult to produce (*mp* of the hexahydrate 89 °C). Con-

centrated magnesium nitrate solutions (e.g., from MgCO₃ and 60% nitric acid) are used for the production of highly concentrated nitric acid.

Naturally occurring magnesium silicates include asbestos and talc. Materials for electrical insulation are also based on magnesium silicates. A series of refractory ceramics are based on magnesium.

Organomagnesium compounds are also known, the most important of these being the Grignard reagents which play an important role in synthetic organic chemistry.

20.11.1 Magnesium Carbonate

Properties. *Anhydrous magnesium carbonate*, MgCO₃, occurs naturally as magnesite which is the starting material for the production of magnesia, MgO. Magnesium carbonate is also synthesized by reacting Mg(OH)₂ with carbon dioxide at high pressure [53]. Magnesium carbonate begins to decompose at ca. 400 °C, the reaction proceeds rapidly above 550 °C. The compound forms colorless or white to gray, trigonal crystals: lattice constant $a = 0.585$ nm, $\alpha = 103^\circ 20'$, $Z = 4$, cleavage parallel to (10 $\bar{1}$ 1).

Density	2.96 g/cm ³
Mohs hardness	4–4.5
Refractive index	$n_D 1.700$, $n_E 1.509$
Enthalpy of formation (298 K)	–1096 kJ/mol
Dissociation energy (298 K)	+1190 kJ/kg
Solubility in cold water	0.0106%

Barringtonite, MgCO₃·2H₂O, forms colorless triclinic crystals, lattice constants $a = 0.9115$ nm, $b = 0.6202$ nm, $c = 0.6092$ nm; $\alpha = 94.00^\circ$, $\beta = 95.53^\circ$, $\gamma = 108.87^\circ$; $Z = 4$; refractive index 1.458, 1.473, 1.501; density 2.83 g/cm³.

The mineral *nesquehonite*, MgCO₃·3H₂O, occurs as colorless to white crystals. This carbonate can also be synthesized by carbonation of Mg(OH)₂ at atmospheric pressure. Density 1.84 g/cm³, *mp* 165 °C (decomp.), solubility in cold water 0.129%.

Lansfordite, MgCO₃·5H₂O, forms white monoclinic crystals, density 1.73 g/cm³. The natural mineral hydromagnesite, 4MgCO₃·Mg(OH)₂·4H₂O, forms white monoclinic

crystals, density 2.25 g/cm³ [54]. The synthetic product is known as *magnesia alba*.

Other MgCO₃-containing minerals include *huntite*, CaCO₃·3MgCO₃ [54] and *dolomite*, CaCO₃·MgCO₃. Dolomite is a rock-forming mineral and is much more common than magnesite. It is burned to form sintered dolomite (for refractory bricks) and light-burned dolomite (used as a fluxing agent).

Uses. The main use of magnesite is the production of *magnesia*. Small quantities are used as a filler. Plans have been proposed for producing magnesium metal from naturally occurring (cheap) magnesite [55]. The synthetic carbonates are used as fillers for paper, plastics, and rubber and as thickening agents for printing inks. Pharmaceutical-grade magnesium carbonate (*magnesia alba*) is also used in toothpaste and as an antacid. High-purity magnesium carbonate is employed in cosmetics.

20.11.2 Magnesium Chloride

Magnesium chloride, MgCl₂, is the commonest naturally occurring, water-soluble magnesium compound. It is a constituent of many salt lakes and natural brines [56, 57]; sea salt contains 17% MgCl₂. Mineral salt deposits contain the important minerals *carnallite* KCl·MgCl₂·6H₂O, *bischofite* MgCl₂·6H₂O, and occasionally the double salt *tachhydrite* in which the magnesium chloride is combined with calcium chloride (CaCl₂·2MgCl₂·12H₂O). *Tachhydrite* is found in salt deposits in Brazil and the Congo region.

Magnesium chloride is obtained from mineral salt deposits by processing the spent liquors remaining after extraction of potassium chloride and also by direct solution mining; it is also recovered from salt lakes and seawater.

20.11.2.1 Properties

Anhydrous Magnesium Chloride. Anhydrous magnesium chloride forms hexagonal crystals, its physical properties are as follows:

M_r	95.23
mp	713 °C

Refractive index (n)	1.675, 1.59
d_4^{20}	2.41 g/cm ³
Specific heat (c_p) between 0 and 713 °C (mp): $c_p = 0.78011 + 0.20607 \times 10^{-3}(t - 20)$ $- 0.10853 \times 10^{-6}(t - 20)^2$ kJ/kg·K ⁻¹	
Specific electrical conductivity at	
700 °C	1.00 Ω ⁻¹ cm ⁻¹
750 °C	1.09
800 °C	1.17
Solubility in water at	
20 °C	35.3%, 54.6 g/100 g
40 °C	36.5%, 57.5
60 °C	37.9%, 61.0
80 °C	39.8%, 66.1
100 °C	42.2%, 73.0
Solubility in methanol at	
0 °C	15.5 g/100 g
60 °C	20.4
Solubility in ethanol at	
0 °C	3.61 g/100 g
60 °C	5.89

Properties of the Hydrates. Magnesium chloride forms five hydrates whose transformation temperatures and solubilities are given in Table 20.10 (see also Figure 20.19). The most important is the hexahydrate, MgCl₂·6H₂O, which forms monoclinic crystals and is present in mineral salt deposits:

M_r	203.31
mp	117 °C
Heat of fusion	34.3 kJ/mol
Density	1.57 g/cm ³
Refractive index (n)	1.495, 1.507, 1.528
Specific heat at	
48.6 °C	1.415 kJ/kg·K ⁻¹
100 °C	1.537

The penta- and hexahydrates can be dehydrated to the tetrahydrate stage almost without decomposition. On dehydration to the dihydrate, however, hydrolytic decomposition starts. Dehydration of the dihydrate at 240 °C leads to extensive decomposition forming magnesium oxychlorides or oxide. To obtain anhydrous MgCl₂, the dihydrate must be dehydrated in an atmosphere of hydrogen chloride.

Table 20.10: Transformation temperatures and corresponding solubilities of magnesium chloride hydrates.

Hydrate transformation	Temperature, °C	Solubility, g MgCl ₂ /100 g H ₂ O
MgCl ₂ solution → MgCl ₂ ·12H ₂ O	-33.6	27.2
MgCl ₂ ·12H ₂ O → MgCl ₂ ·8H ₂ O	-17.4	47.6
MgCl ₂ ·8H ₂ O → MgCl ₂ ·6H ₂ O	-3.4	52.3
MgCl ₂ ·6H ₂ O → MgCl ₂ ·4H ₂ O	116.8	85.6
MgCl ₂ ·4H ₂ O → MgCl ₂ ·2H ₂ O	181.5	125.7

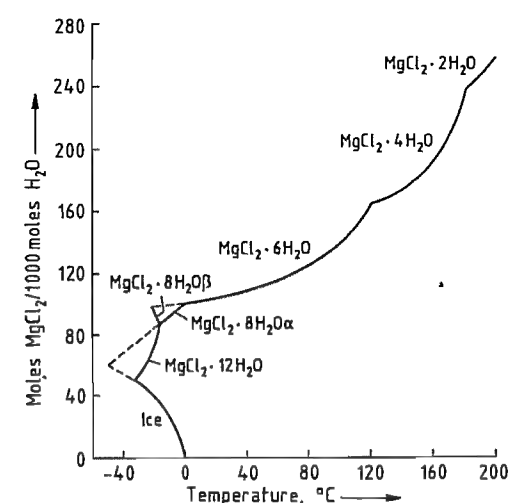


Figure 20.19: State diagram of the system MgCl₂·nH₂O.

Chemical Properties. Magnesium chloride can be decomposed by oxygen to form magnesium oxide and chlorine [58]—the converse of the reaction between magnesium oxide and chlorine to form MgCl₂. With ammonia, MgCl₂ forms ammines that are analogous to the hydrates: MgCl₂·NH₃, MgCl₂·2NH₃, and MgCl₂·6NH₃. Corresponding addition compounds are formed with alcohols and with other organic compounds such as ethers, acetic acid, amines, ethyl acetate, pyridine, hexamethylenetetramine, and dioxane (e.g., MgCl₂·6CH₃COOH).

A series of basic chlorides (magnesium oxychlorides) are formed with magnesium oxide and are of commercial importance as Sorel cement. The following oxychlorides are known: MgCl₂·MgO, MgCl₂·MgO·H₂O, 2MgCl₂·MgO·H₂O, MgCl₂·3MgO·11H₂O, and MgCl₂·3MgO·7H₂O. The compounds MgCl₂·MgO and 2MgCl₂·MgO·H₂O are formed on dehydration of MgCl₂·H₂O at 280–495 °C. Aqueous MgCl₂ solutions are acidic due to hydrolysis. The electrolysis of aqueous MgCl₂ solutions produces magnesium hydroxide and chlorine, whereas electrolysis of anhydrous MgCl₂ yields magnesium metal and chlorine.

20.11.2.2 Raw Materials

Of the three main sources of raw materials for magnesium chloride production, the most important is *seawater*. Magnesium can be directly precipitated from seawater as magnesium hydroxide and converted to magnesium chloride by treatment with chlorine. The residues (*bitterns*) obtained after production of drinking water or sea salt from seawater can also be used. A second large source is the *spent liquor from the potash industry* arising from the processing of hard salts and carnallite-bearing raw materials. A third source is provided by the *salt lakes* in many parts of the world, the Dead Sea and the Great Salt Lake being particularly important.

20.11.2.3 Production

Precipitation of Magnesium Hydroxide from Seawater

If seawater cannot be preconcentrated by solar energy, magnesium chloride salts or solutions can only be produced on a large scale by precipitation as the hydroxide, followed by conversion to the chloride with hydrogen chloride.

The Dow Chemical process is described elsewhere. This process has been used to manufacture magnesium chloride from seawater in large quantities since 1941 in Freeport (Texas). It is an intermediate step in the production of magnesium metal.

Recovery from Spent Liquors from the Potash Industry

The spent liquors obtained after recovery of potassium chloride from carnallite-containing raw salts typically contain (in grams per liter): MgCl₂ 293, MgSO₄ 48, KCl 39, NaCl 26, and H₂O 890. They are used as a raw material for the recovery of magnesium chloride by the Norsk Hydro process.

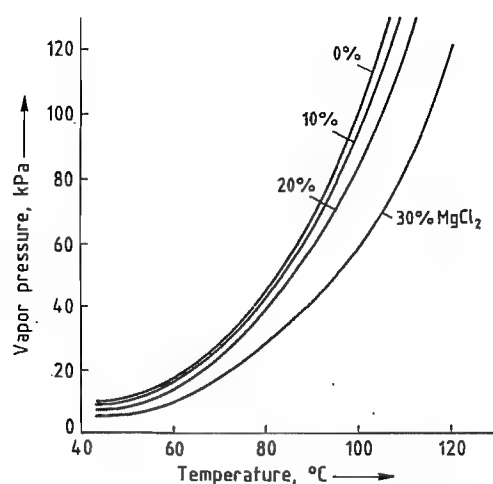


Figure 20.20: Vapor pressure of MgCl_2 solutions as a function of temperature.

Production of Concentrated MgCl_2 Solutions by Kali und Salz AG (Western Germany). The spent liquor contains ca. 280–300 g/L MgCl_2 and is concentrated in a two-stage vacuum evaporator to ca. 460 g/L MgCl_2 . (Vapor pressures of MgCl_2 solutions as a function of concentration and temperature are shown in Figure 20.20).

The solution in the first evaporator stage is heated by the vapor from the second stage to a steady temperature of ca. 55 °C. The second-stage liquor is maintained at 95 °C by heating with steam at 0.1 MPa and the hot, cloudy solution is clarified by removing the salts [carnallite, NaCl , $\text{MgSO}_4 \cdot 5/4\text{H}_2\text{O}$, and impurities such as $\text{Fe}(\text{OH})_3$ and clay] by means of a rotary filter and centrifuge. On cooling carnallite crystallizes out from the solution. The crystallized salts and sludge are sent to the potassium chloride plant where carnallite is decomposed together with carnallite containing crude potash salt. The carnallite is mixed with water or a low- MgCl_2 brine to produce a spent liquor containing 280–300 g/L of MgCl_2 and solid potassium chloride contaminated with sodium chloride and $\text{MgSO}_4 \cdot 5/4\text{H}_2\text{O}$. The cooled MgCl_2 solution is purified by reheating and removing bromine with chlorine. The debrominated solution is neutralized with lime, partly precipitating the sulfate ions in the form of

gypsum. The precipitated sediment is removed. The highly concentrated 32–33% MgCl_2 solution is sold as such or can be processed further to obtain magnesium chloride hydrates.

Production of Concentrated MgCl_2 Solution by the VEB Kombinat Kali (Eastern Germany). The spent liquor from the manufacture of potassium salts has a MgCl_2 content of ca. 260 g/L. The solution is first mixed with synthetic carnallite from the vacuum cooling stage; the MgCl_2 from the carnallite dissolves leaving the undissolved potassium chloride behind. The increased MgCl_2 content (ca. 320 g/L) of the solution lowers the solubility of the alkali-metal salts causing the precipitation of potassium and sodium chlorides. After removal of these salts, the solution is pumped to the second of the two evaporation stages. The preconcentrated solution from the second evaporation stage is pumped to the first evaporation stage where $\text{MgSO}_4 \cdot 5/4\text{H}_2\text{O}$ precipitates together with some langbeinite, carnallite, and sodium chloride. On cooling this solution, (after removal of the salts) in multistage vacuum coolers, synthetic carnallite precipitates. The carnallite is filtered off and recycled to the first step of the process. All the evaporators are of the forced circulation type [59]. The first evaporator stage is operated at 120 °C and heated with steam. The second stage is heated at 80 °C by the vapor from the first stage. The vapors from the second stage are cooled with water.

In a variation of the process, the solution containing 320 g/L MgCl_2 is mixed with part of the product solution (containing 460 g/L MgCl_2). The increase in the MgCl_2 content causes more sodium chloride and carnallite to be precipitated. Evaporation of the solution from the first stages then does not precipitate carnallite or langbeinite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$). Only synthetic kieserite ($\text{MgSO}_4 \cdot 5/4\text{H}_2\text{O}$) and sodium chloride are precipitated and these are removed. The solution produced has a density of 1.340 g/cm³ and contains 460 g/L MgCl_2 , 25 g/L MgSO_4 , 2 g/L KCl , 6 g/L NaCl , 2 g/L CaSO_4 , and 4 g/L Br^- . If this solution is to be

used for the production of magnesium metal, it is debrominated with chlorine. If it is used for production of high-quality sintered magnesia, boron is also removed by boron-selective resins. The boron content decreases from 30 to 5–10 mg/L [60].

Recovery from Raw Salts Containing Carnallite. Patents have been applied for in which pure carnallite or raw salts containing carnallite are decomposed with $\text{C}_1\text{--C}_4$ alcohols, causing the MgCl_2 to pass into the alcohol phase [61]. The alcoholic solution is concentrated by evaporation to an alcohol content of 10% and the hexahydrate is precipitated by addition of water. Alternatively, evaporation is continued until the solution contains 1–2 mol of alcohol per mole of MgCl_2 ; the alcoholate is then thermally decomposed in a hydrogen chloride atmosphere at 400–500 °C.

Evaporation of Seawater and Natural Brines

The direct production of MgCl_2 from seawater or brines by evaporation is only economical where the dilute solutions can be preconcentrated by solar evaporation.

Recovery from the Dead Sea. Magnesium chloride-containing solutions are produced in large quantities by solar evaporation of brine from the Dead Sea. At the Dead Sea Works, carnallite precipitates out and solutions are obtained containing 360 g/L MgCl_2 , 110 g/L CaCl_2 , 7 g/L NaCl , and 5 g/L KCl . Owing to the low vapor pressure of water, solar evaporation only occurs at very low atmospheric humidity levels. After two or three months of evaporation, a density of 1365 g/L is achieved and bischofite separates out [62]. Large quantities of MgCl_2 -containing liquors of this type are now used by Dead Sea Periclase solely for the production of magnesium oxide by thermal decomposition.

In a process patented by the Dead Sea Works for the manufacture of magnesium chloride hexahydrate (bischofite), carnallite or a natural mixture of carnallite and sodium chloride is decomposed in its own water of

crystallization in closed vessels under pressure at 167.5 °C. The potassium chloride remains together with the sodium chloride as a sediment and is removed. The residual solution contains up to 8.2% potassium chloride and 42.3% magnesium chloride. On cooling to 115 °C by flash evaporation, carnallite is precipitated and is fed back into the circulating system. The residual solution contains 1% potassium chloride and consists essentially of bischofite [63].

Recovery from the Kara-Bogaz Gulf, former Soviet Union. Following the isolation of the Kara-Bogaz Gulf from the rest of the Caspian Sea by a dam in 1979, the MgCl_2 content increased to 250 g/L. Research was carried out to find a new method of processing this brine [64]. The brines evaporated in summer contain 25–30% MgCl_2 . When they are cooled in winter, epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) precipitates and is used for producing schönite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$). The liquid phase is used for MgCl_2 production.

Recovery from Spent Liquors after Extraction of NaCl from Seawater. The spent liquors (sea bitters) obtained after extraction of salt from seawater are evaporated in crystallizing pans by solar energy to a density of 1290 g/L. After removing the sodium chloride, the solution is cooled to 5 °C, which can be achieved in winter without energy consumption. Magnesium sulfate (epsomite) crystallizes out with a few impurities and is removed. The bitters are cooled to 0 °C; sodium sulfate (Glauber's salt) crystallizes out and is removed. The solution is then debrominated with chlorine to exclude crystallization of magnesium bromide in subsequent processing. After neutralizing with potassium hydroxide, the liquor is heated to 125 °C. On cooling to 100 °C, a crude potassium-containing salt mixture separates out that consists of langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$) and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$), with some kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and sodium chloride. On further cooling to 20 °C, carnallite crystallizes out which can be treated with water to form a MgCl_2 -con-

taining solution and solid potassium chloride [65].

Recovery from the Great Salt Lake. For the National Lead Industries process, see Section 20.5.1.1. In the process operated by the Great Salt Lake Minerals Chemical Corporation, a 35% MgCl_2 solution is first produced by solar evaporation, and this is then subjected to vacuum evaporation until bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and hydrated MgSO_4 are precipitated. Proposed further treatment consists of heating the crystals to 120–150 °C to redissolve the bischofite and allow removal of magnesium sulfate. The bischofite can then be crystallized out [66]. Alternatively, the solution can be maintained at 120 °C until the magnesium sulfate content decreases to < 20 g/L as a result of crystallization of kieserite. The bischofite is then crystallized by vacuum evaporation at 90 °C [67].

Recovery from Naturally Occurring Brines with High CaCl_2 Contents. Up to the end of World War II, the Dow Chemical Company used underground brines from Midland (Michigan) and Marysville for bromine production and also for the production of MgCl_2 which was electrolyzed to obtain magnesium. The alkali-metal salts were removed by evaporation and crystallization. In an older process the calcium was then separated together with the magnesium as tachhydrite ($2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$) which was converted into $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. In a later process, the solution is reacted with an amount of magnesium hydroxide (produced from magnesite) equivalent to the calcium chloride content. The calcium is then removed as calcium carbonate by treating the solution with the carbon dioxide from the magnesite calcination, and the MgCl_2 is then obtained from the solution.

Today, Dow obtains magnesium chloride for magnesium production only from seawater. The production of bischofite from Michigan brines has been discontinued.

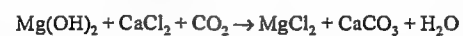
Solution Mining

A 20% MgCl_2 solution is produced in large quantities in the Netherlands from a carnallite salt deposit. It is not used to produce concentrated MgCl_2 solutions, but is almost exclusively converted to magnesium hydroxide [68].

Solution Mining of Carnallite. Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) deposits contain large amounts of magnesium sulfate as well as MgCl_2 . Evaporation of solutions with high magnesium sulfate contents leads to precipitation of double salts containing sodium chloride and magnesium sulfate. In the processing of these solutions, most of the magnesium sulfate is precipitated as langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$) [69], or as schönite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) by precipitation with methanol [70]. In a process developed by the Mines de potasse d'Alsace, a solution containing 320 g/L MgCl_2 can be obtained together with solid potassium chloride by solution mining. The solution used to extract the carnallite from the deposit contains a flotation agent for potassium chloride (C_{12} – C_{20} fatty amines or their salts) and a gas-producing agent such as hydrogen peroxide. The potassium chloride floats and can be pumped out along with the MgCl_2 solution [71]. This production method appears promising, but it is not known whether large-scale development is planned.

Other Methods

Magnesium chloride can be produced from dolomite in combination with soda by the Solvay process. In the early part of World War II at a plant belonging to the Diamond Alkali Corporation in Painesville, Ohio, the dolomite was calcined in rotary furnaces, hydrated, and used to regenerate ammonia from the ammonium chloride solution produced in soda manufacture. Only the calcium hydroxide took part in the reaction. On treatment of the remaining solution with carbon dioxide, a magnesium chloride solution was obtained:



This process is, however, no longer used.

In the Mathison Alkali Works, the calcium chloride solution from the soda process was reacted with calcined dolomite while carbon dioxide was introduced. This process also produced a MgCl_2 solution but has been discontinued. Calcined magnesite or magnesium hydroxide can also be used in the soda process to produce a MgCl_2 solution.

Production of Magnesium Chloride Hydrates

Production of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Bischofite). In a process used by Kali und Salz AG, end bittern from potash production is treated in a single-stage vacuum evaporator to produce a ca. 42% MgCl_2 solution, and is further evaporated in pans with steam at 1.1 MPa. After neutralization with lime and removal of calcium sulfate, synthetic kieserite, and other impurities, the melt is fed onto rotating drum coolers or cooling bands to form a slab which is broken up and marketed. Alternatively, after the initial single-stage evaporation, the solution can be prilled in a prilling tower or spray dried in a fluidized bed [72].

A very pure MgCl_2 hydrate with 4–6 molecules of water can be prepared in 99.9% purity according to a patent of the VEB Kombinat Kali [73]. Carnallite is dehydrated at 180–200 °C and then cooled. The cooled salt is then treated with acetone in which the MgCl_2 dissolves. After removal of the undissolved salt, the hydrate is precipitated from the acetone solution by adding the correct amount of water [73].

In a patent of the Mines de potasse d'Alsace, MgCl_2 is precipitated from solution by addition of 10–25% 1,4-dioxane at room temperature. At lower temperatures the yield of MgCl_2 is increased. The MgCl_2 -dioxane complex separates as a voluminous precipitate that is easy to filter or centrifuge. It can be purified by washing with a little dioxane. The dioxane can be distilled off from the filtrate as an 80% azeotrope and can then be directly reused. The MgCl_2 hydrate can be obtained by washing with water. During drying the remaining diox-

ane (ca. 20–25% of the total) is evaporated off and can also be reused [74].

Production of $\text{MgCl}_2 \cdot (2-3)\text{H}_2\text{O}$. In a process used by Kali und Salz AG, a ca. 33% MgCl_2 solution is heated to 110–130 °C and sprayed into a fluidized bed of magnesium chloride granules at 130 °C. The heating gas is at 400–600 °C. The average residence time of the granules is ca. 30 min. Fines and pulverized oversize granules are recirculated to the fluidized bed. The final product has a water content of ca. 30% [72].

Production of Anhydrous Magnesium Chloride

The Nalco Chemical Company at its plant in Freeport, Texas, produces tetramethyl and tetraethyllead. The Grignard reagents needed as intermediates for the process require a very pure source of magnesium. This is produced by the electrolysis of pure, anhydrous magnesium chloride, for which the following process has been developed.

Ethylene glycol is added with stirring to a 30–35% MgCl_2 solution, the quantity added being sufficient to produce a 10–20% MgCl_2 solution. All the water, including water of crystallization, is then removed by vacuum distillation. The distillate contains < 50 ppm ethylene glycol, and the residual solution contains < 25 ppm water together with all the other salts. Gaseous ammonia is then bubbled through the solution under slight pressure. The mixture is cooled to remove the evolved heat; in practice the temperature is allowed to rise to ca. 70 °C. When the glycol is saturated with ammonia, the hexaammine compound $\text{MgCl}_2 \cdot 6\text{NH}_3$ is formed. Towards the end of the reaction, the mixture is cooled to 15–30 °C, the $\text{MgCl}_2 \cdot 6\text{NH}_3$ precipitates and is filtered off. Any adhering solution is removed by washing with methanol. The ammonia and methanol are then removed in two stages: the methanol and some ammonia are first driven off at 74 °C. The rest of the ammonia is then removed in a calcination furnace at 400 °C [75].

As with the dehydration of carnallite, ammonium carnallite can be dehydrated almost without decomposition at 90–180 °C. It can then be decomposed at 180–400 °C to give ammonium chloride and anhydrous MgCl_2 [76, 77].

In the process developed by Esso Research, a 20–50% solution of magnesium chloride reacts with ammonium chloride in a three-stage fluidized bed. Anhydrous magnesium chloride is produced at 350–550 °C [78].

In another process [79], ammonium carnallite containing $n \text{ NH}_3$ or $n \text{ H}_2\text{O}$ is decomposed at 800 °C. A product with a low magnesium oxide content is obtained. If the starting material contains water of crystallization, some is removed in a first stage, and further dehydration takes place after adding ammonia. After the dehydration, the $\text{MgCl}_2 \cdot 6\text{NH}_3$ is thermally decomposed [80].

A process for the dehydration of magnesium chloride hydrates in a hydrogen chloride atmosphere is described in Section 20.5.1.1.

Purification of Magnesium Chloride Solutions

Calcium ions can be removed from magnesium chloride solutions by adding the stoichiometric amount of sulfate ions [81]. Conversely, sulfate ions can be removed by adding calcium chloride solutions. Calcium and other metallic ions can be extracted with dialkylphosphoric acid in a water-immiscible solvent. This process is used in the production of pure sintered magnesia from solutions of impure magnesites in hydrochloric acid [82]. These solutions can be treated with substances such as MgO , CaO , or $\text{Mg}(\text{OH})_2$ to increase the pH, while simultaneously purging with air or oxygen at 80–90 °C. This removes impurities such as iron, aluminum, and manganese as hydrated oxides or hydroxides. This process is also used in the manufacture of pure sintered magnesia [83].

Materials of Construction for the Evaporation of Magnesium Chloride Solutions

At temperatures up to 110 °C, corrosion is usually prevented by the use of coatings, rubber linings, or plastic reinforced with glass fibers. Heater tubes and distillation trays are usually made of aluminum bronze (AlBz_{5-7}) as used in the potash industry, with a composition of 4–8% Al, 89–96% Cu, and small amounts of Fe, Ni, Mn, As, Si, or Zn. Pumps are made of Ni-Resist D2.

Above 110 °C, and especially in the presence of chlorine and bromine (during debromination), glass and Teflon are suitable, with titanium being used for preheaters and pipework. According to [84] brick-lined steel vessels are used for evaporating MgCl_2 solutions and steam-heated tubes are made of Inconel alloy or stainless steel 347. Monel metal is also used for > 50% MgCl_2 solutions.

20.11.2.4 Environmental and Legal Aspects

Magnesium chloride is a constituent of seawater. In the EEC Regulations (May 4th, 1976) concerning disposal of hazardous substances in lakes and rivers, this substance is not mentioned. However, if large quantities are discharged into lakes or rivers, the concentration can be high enough to injure aquatic organisms and immediate dilution must be carried out. The WHO international standard for drinking water for magnesium is 30 mg/L Mg, or 125 mg/L if the sulfate concentration is < 250 mg/L and the chloride concentration is < 200 mg/L. In the EEC regulation 80/778 EWG the limit for drinking water is 50 mg/L Mg and 25 mg/L Cl^- . In the dehydration of magnesium chloride hydrates, hydrogen chloride occurs in the waste gases due to partial decomposition to magnesium oxide and the concentration must be kept below the permitted limit by use of gas purification equipment. The German TA Luft Regulations specify a maximum of 30 mg/m³ HCl in air. Limits in

Australia are 200–400, in the United Kingdom 150, and in Japan 80–700 mg/m³.

20.11.2.5 Quality Specifications and Analysis

Quality Specifications. Magnesium chloride is available commercially in the form of solutions or solid hydrates. Solutions usually have a MgCl_2 content of 32–33%. A typical solution with a MgCl_2 content of 32–33% has the following approximate composition (in grams per liter):

MgCl_2	430–440
MgSO_4	12–25
KCl	2–3
NaCl	4–6
H_2O	ca. 870

For many applications, however, solutions produced by decomposition of carnallite are used directly; due to transport costs this only applies when the user is close to the supplier.

The most important hydrate sold commercially is the hexahydrate (bischofite) which contains 43–47% MgCl_2 , ca. 51.5% water, ca. 2% alkali-metal chlorides, and, depending on its origin, some MgSO_4 , CaSO_4 , or CaCl_2 . It is supplied in the form of broken pieces or flakes, or as blocks produced by melting and pouring into drums. Another hydrate in granular form contains ca 2–3 mol of water per mole of MgCl_2 and corresponds to 67% MgCl_2 . Anhydrous magnesium chloride is mostly used directly by the producer for electrolytic magnesium production.

Analysis. For quality control the MgCl_2 solutions and the solid hydrates must be analyzed for the following ions Mg^{2+} , Ca^{2+} , K^+ , Na^+ , Cl^- , SO_4^{2-} , and Br^- . In special cases, determination of boron, iron, and other ions may be required.

Magnesium and calcium are titrated complexometrically with ethylenediaminetetraacetic acid (EDTA) [85, 86]. Potassium and sodium are determined by flame photometry [87, 88]. For the determination of sulfate ions, a titration with barium perchlorate solution in a 2-propanol water mixture is carried out with thorin as the indicator [89]. Bromide is deter-

mined gravimetrically by the method of D'ANS and HÖFER [90].

The water content of the hydrates is determined by heating to 450–600 °C or by the lead oxide method [91]. Boron can be determined photometrically with azomethine-H or dianthrimide-1-amine [92, 93] and iron with bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) [94]. Iron can also be determined by atomic absorption spectrophotometry [95].

20.11.2.6 Transportation and Storage

Magnesium chloride solutions can be transported in tank wagons. Owing to their corrosive properties, they should be stored in plastic containers reinforced with glass fiber, but iron vessels can also be used. When a 32–33% MgCl_2 solution is cooled, MgCl_2 hydrates precipitate, gradually forming a sludge. At –33.6 °C the residual solution containing 21.4% MgCl_2 freezes as a eutectic mixture. The hexahydrate is transported in polyethylene sacks or “Big Bags” capable of holding > 50 kg. It is also supplied in the form of broken pieces or solid blocks produced by pouring molten salt in single-journey steel drums. Sealed vessels can be stored almost indefinitely, but, after opening, the material must be used immediately because of its hygroscopicity. All containers must be stored under dry conditions.

20.11.2.7 Uses

Anhydrous magnesium chloride is used chiefly for the electrolytic production of magnesium metal. Large quantities of magnesium chloride solutions are used to produce anhydrous magnesium chloride for this purpose.

An important area of application for the hexahydrate and the hydrate containing 67% MgCl_2 is in the production of Sorel cement. This is made by mixing magnesium oxide with MgCl_2 solutions, and is mainly used as a binder for industrial floorings on account of its high elasticity and bending tensile strength

properties [96]. This binder is also used in the manufacture of abrasive materials and grindstones, and for cementing rock faces during coal mining operations [97]. In combination with wood chippings, it can be used to make lightweight building slabs. Sorel cement mixtures are also used in water- and fire-resistant building materials [98]. They also serve as a binder for granulated fertilizers and in the production of salt licks for animals, where the magnesium also acts as a feed additive, preventing diseases such as grass tetany in cattle that are caused by magnesium deficiency [99].

Another application for MgCl_2 solutions and the hexahydrate is the manufacture of sintered magnesia. A high proportion of the solutions produced in Germany and Israel are used for this purpose. The brines obtained by solution mining in the Netherlands are also used to make sintered magnesia. Magnesium chloride hexahydrate and potassium chloride are used to produce artificial carnallite which is used as a covering flux in the melting of light metal alloys. In the Quentin process used in the sugar industry, the alkali-metal ions in the dilute sugar syrup are replaced by magnesium ions by treating it with an anion-exchange resin, thus reducing sugar losses in the molasses by improving sugar crystallization [100]. The resin is regenerated by adding MgCl_2 solution. In the mineral oil industry, MgCl_2 solutions are used for the drilling fluid in rocks with a high salt content. The low freezing point of the 21% MgCl_2 solution ($< -30^\circ\text{C}$) is utilized to prevent wet bulk materials from freezing to a solid mass, as a de-icing agent in winter, as a ballast liquid for the tires of construction machinery and agricultural vehicles, for fire extinguishing foams at low temperatures, and as brine for refrigeration. It is also used as a heat storage medium in solar heating installations, as an additive in the steel industry, as a coagulant in wastewater treatment, and in the treatment of combustion gases (MgCl_2 solution absorbs HCl and improves the removal of SO_2 by limestone). In the plastics industry it is used in the manufacture of polymerization catalysts. Addition of MgCl_2 also reduces losses of ammonia that is used as a fertilizer [101].

20.11.2.8 Economic Aspects

The total worldwide production of MgCl_2 in 1988 was 1.3×10^6 t. In the world export markets ca. 300 000 t MgCl_2 was handled: ca. 200 000 t in the form of 33% MgCl_2 solutions, and 100 000 t in the form of the hexahydrate. About half of the MgCl_2 solution was used for production of magnesium metal. In addition, approximately 180 000 t MgCl_2 from solution mining brines and 150 000 t MgCl_2 as 33% solution were converted to magnesium oxide; these quantities were reported as material produced but not marketed. A further ca. 700 000 t magnesium chloride was not recorded in any statistics because it was used solely as an intermediate for the production of magnesium by electrolysis.

The most important countries for the production of MgCl_2 solutions and the hexahydrate are given below (excluding magnesium metal producers):

Germany (Kali und Salz AG and VEB Kali)	by-product solutions from the potash industry
Israel	Dead Sea brines
Netherlands	solution mining brines
Japan	sea bitterns from salt production
France	sea bitterns
United States	Great Salt Lake brines
Italy	sea bitterns
China	brines from various salt lakes

Two thirds of the material appearing on the market originates from Germany.

20.11.2.9 Toxicology and Occupational Health

The handling of MgCl_2 hydrates, anhydrous MgCl_2 , or MgCl_2 solutions on a laboratory scale does not present any personal hazards. German chemical regulations do not require any special marking. The LD_{50} (rat, oral) for $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is 8100 mg/kg. Eye protection and rubber gloves should be worn for handling anhydrous MgCl_2 , MgCl_2 hydrates, or solutions. Prolonged contact with concentrated (ca. 35%) solutions or with MgCl_2 dust can cause skin irritation, and possibly allergic skin reactions. In the event of skin problems, the affected area should be

washed with copious amounts of soap and water, followed by treatment with a fat-containing skin cream. In case of contact with the eye, the eye should be washed with water and medical assistance should be obtained.

20.11.3 Magnesium Oxide and Hydroxide [102]

Magnesium oxide seldom occurs as a natural mineral; it is found in contact metamorphic limestone and dolomite, in volcanic ejecta, and in serpentine rocks. It does not form rocks or salt deposits because it is converted to magnesium hydroxide by the water vapor in the atmosphere. The primary sources of industrially produced magnesia are natural magnesite (MgCO_3), seawater, and natural and synthetic brines. Magnesium hydroxide is formed as an intermediate in the production of magnesia from seawater and brines. Magnesia is used in technical applications on account of its high melting point, chemical resistance, high thermal conductivity, low electrical conductivity, and biological activity.

Technical-grade magnesia is mainly sintered to form sintered magnesia (also known as magnesia sinter, dead-burned magnesia, or sintered magnesite) which is used primarily as a refractory material and in the steel industry. Large quantities of calcined (decarbonated) material known as caustic magnesia or caustic-calcined magnesia, are produced for use in agriculture and the building industry. Fused magnesia is normally produced by melting caustic magnesia.

Magnesium hydroxide is produced by precipitation of seawater and brines with calcium hydroxide or by precipitation of soluble magnesium salts. Natural deposits are rare and are not currently being mined.

20.11.3.1 Properties

Magnesium oxide, MgO (magnesia, periclase [103]), is stable in an oxidizing atmosphere up

to ca. 2300°C and up to ca. 1700°C in a reducing atmosphere.

Crystal Structure. Magnesia forms colorless, green, or brown, cubic hexoctahedral crystals, space group $O_h^3 - Fm\bar{3}m$, ionic radius of Mg^{2+} 0.078 nm, $a = 0.421$ nm, $Z = 4$, cleavage parallel to $\{100\}$.

Physical Properties

mp	ca. 2800°C
Mohs hardness	5.5–6
Density	3.58 g/cm ³
Refractive index at 589 nm	1.736
Enthalpy of formation (298 K)	–14 900 kJ/kg
Specific heat c_p	
20–200 $^\circ\text{C}$	1.0 kJ/kg $^\circ\text{K}^{-1}$
20–1000 $^\circ\text{C}$	1.2
Thermal conductivity	
pure crystals 300 $^\circ\text{C}$	22 Wm $^{-1}\text{K}^{-1}$
1000 $^\circ\text{C}$	7
technical-grade 300 $^\circ\text{C}$	12
1000 $^\circ\text{C}$	5
Linear thermal expansion coefficient	
room temperature	$6.7 \times 10^{-6} \text{ K}^{-1}$
1000 $^\circ\text{C}$	14×10^{-6}
1800 $^\circ\text{C}$	16×10^{-6}
Modulus of elasticity (sintered magnesia, bulk density 3.51 g/cm ³)	
25 $^\circ\text{C}$	3×10^4 MPa
1000 $^\circ\text{C}$	2.5×10^4
Dielectric constant (30 Hz–1 MHz)	11
Electrical resistivity	
room temperature	$1 \times 10^{14} \Omega \cdot \text{cm}$
500 $^\circ\text{C}$	1×10^{11}
1000 $^\circ\text{C}$	1×10^7
1300 $^\circ\text{C}$	1×10^3

Magnesium hydroxide, $\text{Mg}(\text{OH})_2$ (brucite), starts to decompose at 380°C .

Crystal Structure. Magnesium hydroxide forms ditrigonal scalenohedral crystals with a typical layer structure, space group $D_{3d}^3 - P\bar{3}m$, $a = 0.313$ nm, $c = 0.474$ nm, $Z = 1$, cleavage parallel to $\{0001\}$.

Physical Properties

Mohs hardness	2.5
Density	2.38 g/cm ³
Refractive index	n_e 1.566, n_o 1.581
Enthalpy of formation (298 K)	–15 800 kJ/kg
Dissociation energy (298 K)	+570 kJ/kg
Hydration energy	–386 kJ/kg
Solubility in cold water	0.0009%

Toxicity. Magnesium oxide and hydroxide are not toxic. Precautions for handling dust must be observed when products with a small particle size are used.

20.11.3.2 Production of Magnesium Oxide

Caustic and sintered magnesia are generally obtained from magnesium carbonate or magnesium hydroxide. The production of the latter starting materials is described in the four next subsections. The burning and sintering processes are dealt with in the fifth subsection. The production, properties, and uses of fused magnesia are described in Section 20.11.3.5.

Production from Magnesite [104]

The production of magnesium oxide from magnesite began over 100 years ago in Austria, after the development of processes for the manufacture of steel from high-phosphorus pig iron in crucibles lined with sintered dolomite ($\text{CaO} \cdot \text{MgO}$).

Occurrence of Magnesite. Magnesite is produced from macro- and cryptocrystalline magnesite. Metamorphic *macrocrystalline magnesite* occurs in two Alpine mountain chains in varying degrees of purity. The rocks mainly consist of the isomorphous carbonate mineral (Mg,Fe) CO_3 (breunnerite), whose calcination results in the inclusion of 1–10% Fe_2O_3 in the periclase lattice. In addition, they contain small amounts of dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), calcite (CaCO_3), phyllosilicates (e.g., talc, mica, chlorites, or clay minerals), graphitic particles, and sometimes quartz. Similar magnesite deposits are exploited in Czechoslovakia, in the Pyrenees, in Ural (Satka), South Manchuria (Liaoning), East Brazil, and Canada, both by open-cast and underground mining. The macrocrystalline rocks are always subjected to some form of processing before calcination.

In contrast to the macrocrystalline magnesites, which form extensive or lenticular deposits, *cryptocrystalline magnesite* deposits are irregular and often veined. The rocks are mostly snow white, even if they are not com-

posed of high-purity MgCO_3 . They are regarded as being formed by the alteration of ultrabasic rocks (e.g., serpentines) through the action of water containing carbon dioxide. Deposits of this type occur in former Yugoslavia, Greece (Chalkidike and Euboa), Turkey, India, Nepal, and South Africa. They contain chalcedony (finely divided SiO_2), various magnesium silicates, and dolomite as accompanying minerals. The deposits are exploited mainly by open-cast mining, but also by underground mining.

Sedimentary deposits of cryptocrystalline magnesite have been identified in the last 20 years. They are often associated with deposits of hydromagnesite and huntite. The sedimentary deposits are formed in semi-arid basins associated with strongly weathered ultrabasic rocks. The material washed into the basin dissolved and then recrystallized on the basin rim, mostly in the form of porous concretions. A more recent formation of this type has been found in Southwest Turkey [105], while an older deposit has been reported in North Greece [106, 107]. A large deposit of this type was discovered in Australia (Kunwarara) in 1985. The Queensland magnesia project has been planned for the production of sintered and fused magnesia [108, 109].

Magnesite Beneficiation. The insufficient purity of the magnesite and the stringent specifications for the uniformity of sintered magnesia mean that beneficiation of the magnesite is usually necessary. The steps used in the beneficiation process depend on the ore being processed and the required carbonate purity.

The highest quality magnesites, particularly those for refractory applications, are needed for a magnesia product with a high MgO content, a $\text{CaO}:\text{SiO}_2$ mass ratio of 2–3, and low contents of Fe_2O_3 and Al_2O_3 . The presence of accompanying, low-melting minerals can adversely affect the properties of the sintered magnesia (Table 20.11).

Table 20.11: Minerals accompanying periclase in sintered magnesia.

Mineral	Formula	Abbreviation ^a	C:S ^b	mp, °C
Forsterite	$2\text{MgO} \cdot \text{SiO}_2$	M_2S	0	1890
Monticellite	$\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$	CMS	0.94	1495
Merwinite	$3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	C_3MS_2	1.40	1575 (decomp.)
Dicalcium silicate ^c	$2\text{CaO} \cdot \text{SiO}_2$	C_2S	1.87	2130
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S	> 1.87	1900 (decomp.)
Magnesioferrite	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$	MF		1750
Dicalcium ferrite	$2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	C_2F	> 1.87	1435

^a Abbreviations as used in the cement industry: M = MgO , C = CaO , S = SiO_2 , F = Fe_2O_3 .

^b Mass ratio of CaO to SiO_2 (dissolution of small amounts of CaO in the MgO is neglected).

^c Several modifications.

Preliminary sorting of the ore can be achieved by *selective mining*. The ore is then subjected to *selective coarse grinding* in impact crushers. The tailings can be separated from the ore by taking advantage of the difference in hardness; the ore is selectively crushed and removed by screening. Crushing is usually performed in several stages. The final particle size for calcination in shaft kilns is 20–200 mm, while a particle size of 2–60 mm is required for the more commonly used rotary kilns.

The difference in color between the cryptocrystalline magnesite ore and the tailings is usually so pronounced that sorting can be carried out by hand on a conveyor belt or with an automatic optical system.

The coarsely ground material is often washed and subjected to wet desliming to remove fine particles. Ore that is intended for direct caustic calcination is separated from fine material (often lamellar silicate particles) by screening.

When the magnesite is not intimately intergrown with its accompanying minerals, lump material for rotary kilns can be sorted by gravity separation. This is carried out in one or two stages in a dense-medium separator or cyclone to give particles of sizes of 10–40 or 4–60 mm respectively. Since the differences in density are small (magnesite 2.95–3.05, dolomite 2.90, calcite 2.70, lamellar silicates 2.5–2.95, quartz 2.65, graphite 2.1–2.2 g/cm^3), separation depends on exact control of the density. Finely divided ferrosilicon is generally used as the dense medium; the impurities are removed as floats. The throughput in modern plants is 50–150 t/h.

If the degree of intergrowth of the magnesite with its accessories lies in the range 0.03–1 mm, separation can only be achieved after thorough grinding of the ore (particle size below ca. 0.2 mm) to expose the accompanying minerals. The currently most effective separation and enrichment process for this material is *flotation* which exploits the differing wettabilities of the various minerals. The process must be optimized for each deposit.

The magnesite is finely ground in rod or ball mills and should have as narrow a particle size distribution as possible (ca. 0.09 mm for coarsely crystalline magnesite). This is achieved by combining milling with gravity classification and classification cyclones. Flotation is usually preceded by desliming to remove the finest particles, which would otherwise cause problems in the flotation step.

The removal of talc, $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$, is straightforward. Upon mixing with air in the presence of weak collectors–frothers (e.g., pine oil and primary aliphatic fatty amines), the talc particles float to the surface on bubbles and are removed by skimming.

The main problem in flotation is the separation of magnesite from dolomite, calcite, and silicates other than talc. Separation is achieved by *direct magnesite flotation* which entails the use of nonspecific, anionic collecting agents (that also act as frothers) and selective depressing agents for dolomite, calcite, and silicates. The flotation cells have a capacity of 0.5–3 m^3 . The operational conditions in the flotation cells must be optimized (temperature, pH value, reagent dosing). In large-scale flotation plants, several series of cells are run in parallel. The typical throughput of a series

is 20 t/h of magnesite, corresponding to 60 m³ of suspension with a density of 1.25 g/cm³.

The magnesite concentrate is removed as a foam, then thickened, and brought to a residual water content of 8–12% in centrifuges or filters. The product is then briquetted and burned. The waste slurries from the desliming and flotation stages are treated in thickeners, filters, and settling basins.

An important sorting process for high-iron sintered magnesite is *magnetic separation*. The isomorphous inclusions of iron in the magnesite crystal cannot be removed by mechanical separation. After sintering and subsequent cooling, they are converted to magnetic magnesioferrite (MgO·Fe₂O₃), either in the periclase lattice or at its crystal boundaries (Figure 20.21B). Calcite and dolomite usually do not contain iron in the carbonate lattice; the calcination of large crystals gives large pieces of very pure, usually only lightly sintered, nonmagnetic CaO or CaO and MgO. These oxides can be separated, together with nonmagnetic silicates, from the sintered iron-rich magnesite in magnetic drum separators.

Recently developed magnets are reported to be able to remove pieces of sintered magnesite.

Table 20.12: Typical analyses of sintered magnesite.

Type of magnesite ^a	Composition, %						Bulk density ^b , g/cm ³	Theoretical density, g/cm ³
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	B ₂ O ₃		
1	91.5	1.5	4.5	1.1	1.4	0.14	3.27	3.57
2	89.0	2.4	0.5	7.8	0.3		3.26	3.64
3	88.0	2.5	0.6	8.6	0.3	< 0.01	3.38	3.65
4	91.3	1.9	0.5	6.0	0.3	< 0.01	3.40	3.63
5	98.0	0.7	0.7	0.2	< 0.2	0.30	3.28	3.57
6	97.2	1.9	0.5	≤ 0.2	0.2	0.05	3.43	3.57
7	96.4	2.0	1.1	0.4	< 0.1	< 0.01	3.43	3.57
8	97.2	2.0	0.4	0.3	≤ 0.1	< 0.01	3.42	3.57
9	98.5	0.7	0.15	0.5	< 0.1	0.015	3.45	3.58
10	99.0	0.7	0.1	< 0.1	< 0.1	< 0.01	3.43	3.58

^a 1) Lump sintered magnesite with a high silicate (and iron) content.

2) High-iron sintered magnesite produced from flotation concentrate.

3, 4) Lump high-iron sintered magnesite.

5) Sintered magnesite produced from seawater type 11 (C:S = 1:1).

6) Sintered magnesite produced from seawater type 31 (C:S = 3:1).

7) Lump low-iron sintered magnesite.

8) Low-iron sintered magnesite with large crystals (LC) produced from flotation concentrate.

9) Sintered magnesite produced from MgCl₂ brine.

10) Sintered magnesite produced from pyrohydrolyzed MgCl₂.

^b According to DIN 51065, part 2.

sia with a somewhat higher iron content from low-iron sinter [108].

Table 20.12 lists typical analyses of sintered magnesite produced from natural magnesite (types 1–4, 7).

Production from Seawater [110, 111]

Few deposits of pure or easily accessible magnesite were known up to the mid-1980s. In the 1960s the increasing demand for sintered magnesite as a refractory lining material in the steel industry stimulated new developments in methods for production of magnesite from seawater. This method was first introduced on a small scale in 1865 on the French Mediterranean coast. Since the 1930s it has been employed on a large scale in the United States and England (Hartlepool).

The composition of seawater is given in Table 20.13 [112]. Calculations show that 470 m³ of seawater are required to produce 1 t of MgO, in practice 600 m³ are needed. The process is based on the precipitation of magnesium hydroxide (solubility in water 0.0009%) by addition of calcium hydroxide (solubility 0.185%):

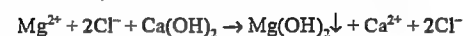


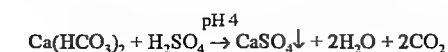
Table 20.13: Composition of seawater [112].

Cation	Concentration		Anion	Concentration	
	g/kg	mmol/kg		g/kg	mmol/kg
Sodium	10.47	455.0	chloride	18.97	535.1
Potassium	0.38	9.7	bromide	0.065	0.81
Magnesium	1.28	52.5	sulfate	2.65	27.6
Calcium	0.41	10.2	bicarbonate	0.14	2.35
Strontium	0.013	0.15	borate	0.027	0.44

Freshwater from rivers contaminated with suspended material must not flow into the seawater used for magnesite production. Furthermore, the seawater to be extracted should not be mixed with already extracted seawater, this requires a suitable topography and tidal currents that run parallel to the coast. A supply of freshwater (> 40 m³ per tonne MgO) is required to wash the Mg(OH)₂ and to produce the milk of lime. High-purity limestone or dolomite deposits should be available in the vicinity; they are calcined and slaked to provide Ca(OH)₂ as the precipitating agent and should therefore contain minimal quantities of elements that form insoluble carbonates, sulfates, etc. The MgCO₃ in dolomite is converted to Mg(OH)₂, and thus provides a further source of magnesite.

Production of Precipitating Agent. The limestone or dolomite is thoroughly washed, crushed, and calcined at > 1400 °C in a rotary or shaft kiln. The CaCO₃ must be completely decarbonated to CaO (< 0.2% CO₂), but should be lightly burned, and should contain minimal amounts of sulfur and other contaminants. In order to achieve rapid, complete reaction of the seawater, the calcined lime (quicklime) or dolomite (dolime) is ground, slaked to form Ca(OH)₂ and then converted into milk of lime or dolomitic slaked lime (containing ca. 20% solids).

The seawater is pumped to the plant and suspended material is removed. Seawater contains dissolved carbon dioxide and must therefore be treated with sulfuric acid to prevent the subsequent formation of insoluble calcium carbonate on addition of Ca(OH)₂:



The freshwater is also partially decarbonated.

To ensure maximum removal of carbon dioxide, the water is pumped through a trickling installation into the reactor containing the milk of lime. The water leaving the reactor is pumped back into the sea; it has a low magnesium content, a high calcium content, and a pH of 10.5. In modern plants using the overliming process (see below) the extracted water is first pumped into settling basins where the excess lime is diluted with fresh seawater to precipitate more Mg(OH)₂ and to lower the pH to more ecologically acceptable values.

Precipitation. The aqueous suspension of finely precipitated Mg(OH)₂ is seeded with larger Mg(OH)₂ crystals in large, flat settling tanks to convert it into a thick, dense slurry for filtering. The slurry is removed from the bottom of the tank and fed into tanks where it is washed with decarbonated seawater and decarbonated fresh water to remove most of the alkali metal, chloride, and other ions. The water content of the Mg(OH)₂ slurry is then reduced to < 50% by filtration (vacuum disk or drum filter). The product is used as a starting material for caustic and sintered magnesite.

Unless specially treated, caustic and sintered magnesite produced from seawater usually contain ca. 0.2% B₂O₃ and small amounts of CaO, SiO₂, Al₂O₃, and Fe₂O₃ derived from the limestone or wastes in the seawater. The contaminants and the CaO:SiO₂ (C:S) ratio have a pronounced effect on the behavior of the magnesite during sintering and in its subsequent applications. The C:S ratio is therefore adjusted to the desired value (3–4 or more for the high-quality sinters used in oxygen metallurgy). The B₂O₃ content of the magnesite is also generally lowered to ca. 0.05% by using a 5–12% excess of lime for precipitation (overliming); this increases the pH to 12 and minimizes the adsorption of boron. Addition of small quantities of Na₂CO₃ prior to sintering further decreases the B₂O₃ content to 0.03% due to the formation of volatile sodium borate during sintering. Prolonged sintering at the maximum temperature decreases the B₂O₃ content. Ion exchange can also be used to

lower the boron content of the seawater and thus of the sintered product.

Typical compositions of the two most common types of magnesia sinter derived from seawater are given in Table 20.12 (types 5 and 6).

Production from Brines

Precipitation of Magnesium Hydroxide. Large marine and terrestrial salt deposits were formed in various geological periods. Fossil mineral salt deposits have been mainly mined for their potassium salts: magnesium salts or magnesium brines are obtained as waste or as a by-product.

Magnesium salts are formed in arid areas by evaporation of brines in flat basins, their composition often differs from those obtained from seawater. Magnesia is obtained from magnesium (potassium) brines of varying origin:

- Synthetic brines produced during solution mining (e.g., Veendam, Netherlands)
- Spent liquors obtained in salt production from natural brines (e.g., Dead Sea potash production; Laguma de Rey, Mexico, sodium sulfate production)
- Spent liquors obtained in salt production from salt deposits (e.g., Teutschenthal, Germany)

In the Netherlands (Veendam Ost-Groningen), purified freshwater is forced into an anticline at a depth of 1500 m to dissolve the bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) [113]. The brine is then pumped to the surface and contains 20% MgCl_2 and small amounts of alkali chlorides and MgSO_4 . After removal of the sulfate, the magnesium is precipitated as $\text{Mg}(\text{OH})_2$ with dolomitic slaked lime, thickened, and then sintered. The advantage of this deposit is that the bicarbonate and boron contents of the resulting brines are much lower than those of seawater and do not have to be removed by complex methods.

Pyrohydrolysis of Magnesium Chloride [114, 115]. In pyrohydrolysis, metal (M) ha-

lides (especially chlorides) are thermally decomposed in the presence of superheated steam at 300–1000 °C to give a pure, fine metal oxide precipitate:



Pyrohydrolysis was originally used to recover hydrochloric acid in the pickling of steel but it can also be employed for the large-scale production of metal oxides. Magnesium oxide is produced from natural or synthetic MgCl_2 brines. Complete hydrolysis of MgCl_2 by conventional methods is not possible because evaporation leads to precipitation of bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) which, on further heating, melts or dissolves in its own water of crystallization. Complete pyrohydrolysis of MgCl_2 is achieved in a spray reactor without hydrolysis of CaCl_2 and alkali chlorides (Aman process).

Table 20.14: Composition (in grams per liter) of brines used in the production of magnesia by the spray roasting method.

Component	Natural brine	Brine for pyrohydrolysis after KCl extraction
Mg^{2+}	41	102
Na^+	40	2
Ca^{2+}	17	9
K^+	7.5	2
Cl^-	215	319
Br^-	5	6
SO_4^{2-}	0.7	
Total	326	440
MgCl_2	163	400

The *Aman process* has been used since 1973 in an industrial plant with a current capacity of 70 000 t/a near the Dead Sea. The starting material for this process is the spent liquor (brine) obtained after extraction of KCl from a magnesium- and alkali-chloride-rich natural brine. The compositions of these brines are given in Table 20.14.

The brine is purified to remove bromide and traces of boron and then fed via steel pipes into the spray nozzles of the reactor. It is sprayed into the cylindrical, externally insulated reactor at ca. 600 t. The reactor is lined with refractories, it also has a conical base and tangentially positioned burners which ensure rotating circulation of the reactants. The exhaust gases leave the top of the reactor at

450 °C. The water evaporates from the atomized brine droplets leaving a perforated chloride crust which reacts with the steam to form MgO and HCl . The hollow spherical MgO agglomerates are removed from the bottom of the reactor via a gas lock, together with non-pyrolyzed, water-soluble potassium, sodium, and calcium salts.

The crude product is washed with water and hydrated in a stirred tank, and then concentrated in a thickener. The resulting slurry is difficult to filter and is washed and dewatered in a two-stage vacuum drum filter. The calcined product typically contains $\geq 99.5\%$ MgO , $< 1\%$ CaO , $\leq 0.05\%$ SiO_2 , $\leq 0.05\%$ Fe_2O_3 , $\leq 0.005\%$ Al_2O_3 , and $\leq 0.01\%$ B_2O_3 ; its specific surface area is 2–50 m^2/g , the loose bulk density ranges from 0.8 to 0.2 g/cm^3 .

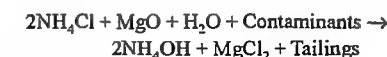
Most of the MgO dust in the hydrogen chloride exhaust gas is removed with a cyclone. The hot gas is then used to heat the fresh MgCl_2 solution in a wash recuperator where any remaining MgO dust is collected. The HCl gas is scrubbed with water in an absorption column. After removal of the combustion gases and steam, 20% hydrochloric acid is obtained which is used to dissolve local phosphate deposits; this makes the process economically viable.

Pyrohydrolysis of Magnesium-Containing Waste. The principle of the above method can also be used for the pyrohydrolysis of chloride solutions obtained from impure magnesium minerals such as magnesite, tailings, dust, asbestos, talc, and other magnesium silicate waste [116]. The hydrochloric acid by-product is recycled within the process (former Yugoslavia, Nepal, Austria, and Germany).

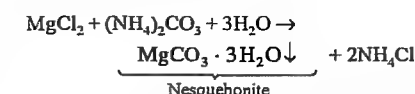
The magnesium is dissolved with hydrochloric acid in a two-stage process. Neutralizing agents (filter dust or crude MgO), oxidizing agents (air, chlorine gas), and sulfate ions are then added. Heavy-metal hydroxides, calcium sulfate, and other contaminants precipitate out and are filtered off to leave a MgCl_2 solution that is concentrated in a vacuum evaporator and sprayed into the reactor.

Miscellaneous Processes

Sulmag II Process [117]. The Sulmag II process was developed by Sulzer for producing light-burned caustic magnesia in a gas suspension kiln from low-magnesite ores. Dissolved magnesium chloride is obtained by selective extraction with recycled NH_4Cl solution:



After filtration and washing, needle-shaped crystals of nesquehonite are precipitated out in the reactor and filtered off:



Caustic magnesia with a high specific surface area is obtained by directly heating the nesquehonite with oil or gas and briquetting while still hot. The product is then sintered. This process is reported to produce significant energy savings and is environmentally favorable due to the almost complete recycling. A pilot plant has been in operation in Switzerland for several years and a plant designed to produce 30 000 t/a of sintered magnesia is under construction for Tamilnadu Magnesite in India.

Other Processes. Processes have been described in which dolomite is decarbonated to form a mixture of CaO and MgO and the CaO is then chemically extracted. Patents also describe the partial decarbonation of dolomite, slaking of the MgO , and recarbonation. The product consists of large nesquehonite crystals ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) which are separated from the microcrystalline CaCO_3 by flotation. The accessory calcite and dolomite can also be extracted from magnesite rocks because they are readily soluble in acid.

Magnesia can also be prepared from Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) but this technique is not used industrially at present.

MgO and CaO Production by Sintering of Dolomite. Complete decarbonation of dolo-

mite theoretically leaves a finely crystalline mixture of MgO (42%) and CaO (58%).

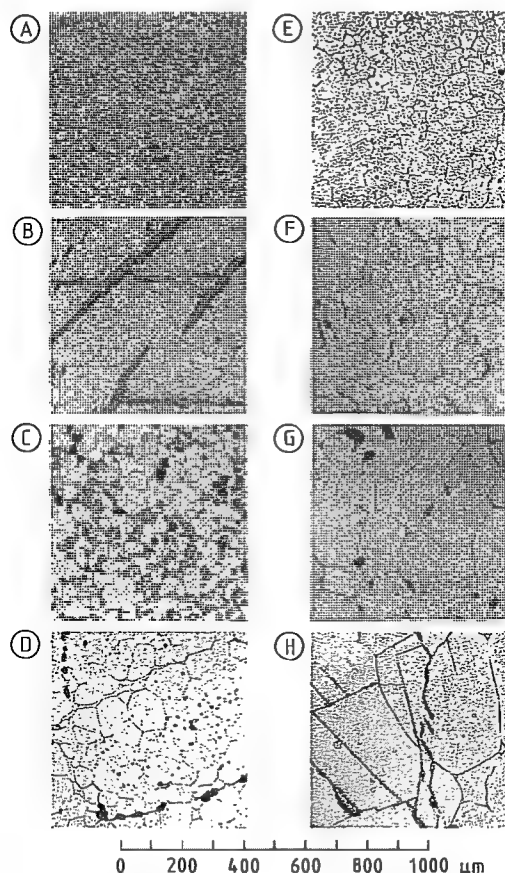


Figure 20.21: Polished sections of sintered dolomite (A), sintered magnesite (B–G), and fused magnesite (H). A) Sintered dolomite: white areas are MgO, gray areas CaO, and black areas pores; B) High-iron magnesite sintered in lumps: white domains are $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and $\text{MgO}\cdot\text{Fe}_2\text{O}_3$, dark gray areas are pores that run parallel to the carbonate cleavage planes (type 4 in Table 20.12); C) Briquetted high-iron sintered magnesite with a high porosity (type 2 in Table 20.12); D) Low iron magnesite sintered in lumps (type 7 in Table 20.12); E) Seawater magnesite "31" (type 6 in Table 20.12); F) Sintered magnesite from brine (type 9 in Table 20.12); G) Low-iron C sintered magnesite (type 8 in Table 20.12); H) Fused magnesite with periclase cleavage planes.

Since large supplies of natural, high-purity dolomitic rocks are available, removal of contaminants by beneficiation is not economical. The high-purity lump dolomite is calcined, and sintered in a rotary or shaft kiln. In a spe-

cial procedure the dolomite is decarbonated, briquetted, and sintered at a lower temperature than the lump material to give a high-density product. The CaO and MgO crystals in sintered dolomite lie directly adjacent to one another (Figure 20.21A); despite the intense burning they are much smaller than those of sintered magnesite because they mutually hinder one another's crystal growth.

Calcination of Caustic and Sintered Magnesia

Caustic magnesia is a very reactive, finely crystalline material that is produced by calcining MgCO_3 or $\text{Mg}(\text{OH})_2$ slightly above the decomposition temperature. The decomposition curves for $\text{Mg}(\text{OH})_2$, MgCO_3 , and $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$ are shown in Figure 20.22. Caustic magnesia may be the end product of magnesite production or may be further burned to give sintered magnesia.

Caustic magnesia is produced industrially by calcining lump MgCO_3 (up to 50 mm) or liner material at 600–1000 °C in shaft, rotary, or multiple-hearth (Herreshoff) kilns. Heat-exchange kilns are also employed. In the case of $\text{Mg}(\text{OH})_2$, dewatered filter cakes are usually calcined in lump form at ca 950 °C in multiple-hearth kilns. These kilns generally contain ten shelves (hearth), one above the other; each hearth is provided with four burners in the vertical cylindrical kiln wall. The material is fed continuously into the top of the kiln and its residence time can be adjusted via the rake that rotates above each hearth. The calcining conditions must be carefully adapted to the contaminants in the feed, otherwise overburning results in excessive growth of the reactive MgO crystallites which lowers their activity. In modern gas suspension furnaces, $\text{Mg}(\text{OH})_2$ or flotation concentrate can be converted into homogeneous caustic magnesia; energy consumption is low [118].

Caustic magnesia was formerly produced exclusively from cryptocrystalline magnesite with a low iron content but is now also obtained from all types of magnesite and $\text{Mg}(\text{OH})_2$. Its MgO content ranges from ca 65

to 99%, and may even reach 99.9%. The magnesia is often ground prior to use. Extremely reactive caustic magnesia may have a surface area of up to 160 m²/g.

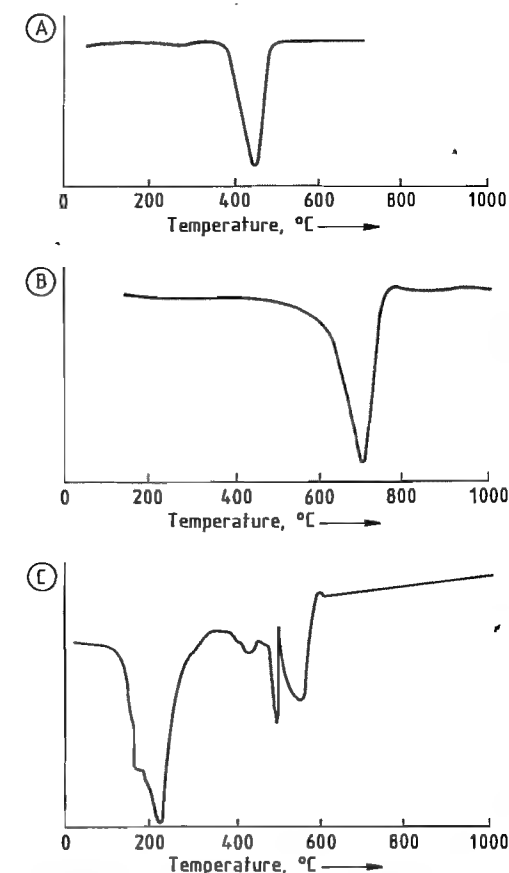


Figure 20.22: Differential thermal curves for $\text{Mg}(\text{OH})_2$ (A), MgCO_3 (B), and $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$ (C) [133].

Depending on the calcining temperature, the product is termed *light burned* (870–1000 °C) or *hard burned* (1550–1650 °C). Light-burned caustic magnesia becomes hydrated in cold water and is soluble in dilute acid. It has a loose bulk density of 0.3–0.5 g/cm³ and a specific surface area (BET) of 10–65 m²/g. Hard-burned caustic magnesia has a loose bulk density of 1.2 g/cm³ (bulk density 2 g/cm³).

Sintered Magnesia. Most (ca. 85%) MgCO_3 and $\text{Mg}(\text{OH})_2$ is converted into sintered mag-

nesia (also known as magnesia clinker or dead-burned magnesia, Figure 20.21B–G). Typical analyses and densities of sintered magnesia are given in Table 20.12. Uses are described in Section 20.11.3.3. Sinter quality depends not only on chemical composition but also on the bulk density or porosity; a high density gives a better product. Sintering capability decreases considerably with increasing purity, making a high density difficult to achieve. In the early 1960s lump magnesite with a low iron content could not even be sintered to a density of 3.40 g/cm³ (porosity ca. 5 vol%). Although some briquetted, low-iron, C₂S-containing sinters have densities of up to 3.46 g/cm³ (porosity ca. 3.5 vol%), the density is usually in the range 3.35–3.40 g/cm³. The final bulk density of the sinter depends on chemical composition, sintering temperature and time, and the degree of compression of the material prior to sintering (briquetting is therefore used and not pelletizing or granulation). The material is usually sintered in lump form.

Caustic magnesia (preferably hot, 200–500 °C) is compressed into briquettes on high-pressure roller presses (pressure 4–15 t/cm²). The briquettes are then screened and dried or hardened. The screened fines are mixed with fresh caustic magnesia and briquetted.

Binding and adhesive agents are added to fine *magnesite flotation concentrates* prior to briquetting; magnesium sulfate solution, sulfuric acid, lignin sulfonates, and reactive MgO flue dust are usually used. Magnesite concentrates are also used to produce double-burned sinter. Here the concentrates are first calcined to reduce the mass and the resulting gas pressure; they are then briquetted and sintered.

In some cases dewatering of *magnesium hydroxide slurries* is so efficient (high-performance filter presses) that pieces of the hard filter cake can be fed directly into a rotary kiln. This saves a considerable amount of energy and the sintered magnesia product usually has a sufficiently high bulk density. In most modern plants, however, the hydroxide slurry is first calcined and then briquetted.

Shaft kilns are heated with coke, gas, or oil (with or without oxygen) and must be fed with

large pieces of material due to the pattern of gas circulation and movement of material within the shaft. Today, shaft furnaces can be better controlled than was the case a few years ago [119]. Smaller lumps (0.5–60 mm, product 0–30 mm) are used in rotary kilns to minimize abrasion and guarantee even movement of the material from the rotating kiln wall. Rotary kilns are generally oil- or gas-fired, sometimes with addition of coal dust or petroleum coke. Depending on the content of fluxing agents, sintering is performed at 1700 to > 2000 °C for 2–15 h (rotary kiln) or ca. 20 h (shaft kiln). The sinter from rotary kilns is generally homogeneous but has a smaller particle size and contains more dust than that from shaft kilns; this can lead to undesirable, round particles and an excess of fines during brick production. Cryptocrystalline magnesite with a low content of fluxing agents gives a sinter with a needle-like structure also after sintering in a rotary kiln.

Energy consumption for the burning of high-quality sintered magnesite from various starting materials depends on kiln design and the water content of the $\text{Mg}(\text{OH})_2$ slurry; typical values are as follows (MJ/kg MgO):

Magnesite: single-stage burning (magnesite → sinter)	4.5–12
Magnesite: double-stage burning (magnesite → caustic magnesite → sinter)	8–16
Seawater magnesite [$\text{Mg}(\text{OH})_2$ → caustic magnesite → sinter, value includes energy required for production of precipitation agent]	22–32
Sulmag II process	23
Magnesite produced by pyrohydrolysis	40

In an effort to improve sinter quality, manufacturers first turned their attention to increasing the size of the periclase crystallites by adding sinter-promoting agents, such as ZrO_2 . Burning conditions were subsequently modified. In larger crystallites the MgO is less easily reduced by carbon at high temperatures (e.g., in magnesite graphite bricks; see also Figure 20.21G).

Modification of Sinter Composition. In the case of concentrates, slurries, or caustic magnesite, the final composition of the sinter can be modified by mixing in small amounts of additives such as CaO , SiO_2 , and Fe_2O_3 prior to briquetting. Magnesite concentrates obtained

by flotation and fine $\text{Mg}(\text{OH})_2$ or MgO can also be mixed with large quantities of other fine substances (primarily chromium ores, calcined lime or dolomite), briquetted, and sintered to form coolinker. In refractory bricks made from pure sintered magnesite and low-silicate chromium ores, the chromium ore only becomes fully integrated with the periclase at high temperature (≥ 1700 °C) and in a suitable atmosphere. In briquettes made from magnesite and fine chromium ore, however, sintering results in complete dissolution of the mixed spinels of the ore in the periclase. On cooling, fine crystalline spinels or skeleton crystals precipitate in the periclase; some idiomorphic spinels ($\text{Mg,Fe}^{2+}\text{O}(\text{Cr,Fe}^{3+},\text{Al})_2\text{O}_3$) are evenly deposited between the periclase crystallites.

20.11.3.3 Uses

The use of magnesium oxide and hydroxide as intermediates in the production of magnesium metal is described elsewhere.

Use of Sintered Magnesite as a Refractory

Oxides are best suited as “vessel linings” for most industrial high-temperature processes. Magnesium oxide has the highest melting point of the moderately priced oxides and is therefore an important raw material for refractory bricks and other materials. It is the only material apart from ZrO_2 that can withstand long-term heating above 2000 °C. Refractory construction materials based on magnesite (with chromium ore or CaO) are also resistant to neutral and basic slags and gases.

The boom in the production of low-iron sintered magnesite occurred after it was discovered that the use of refractory magnesite linings in steelmaking vessels (open-hearth furnace, electric arc furnace, and basic oxygen furnaces) allowed phosphorus and sulfur to be removed in the basic slag.

Sintered magnesite is converted into fired bricks by techniques used for traditional ce-

ramics. It is first broken up, ground, and classified. Batches (1 to > 2 t) of individual fractions are mixed with a temporary aqueous binder (e.g., lignin sulfonates) and pressed into bricks of the desired shape weighing up to ca. 35 kg. After drying, the bricks are usually fired at 1500–1800 °C in a tunnel kiln. They have a final porosity of 12–20 vol%.

Bricks (especially those that are to be used in basic oxygen furnaces) may then be *impregnated with pitch* to prevent the slag from infiltrating them and dissolving their surface. Fired magnesite bricks have a high thermal expansion coefficient and a relatively low thermal shock resistance, especially during periodic operation. Fired bricks made from sintered magnesite and chromium ore (or alumina or spinel) are more resistant to thermal shock.

A large proportion of the magnesite bricks are not fired (i.e., do not form a ceramic bond) but are *bonded with pitch or resin*. The individual particle fractions are mixed with hot pitch, compressed into bricks, and tempered at 200–500 °C. When the bricks are used, a coke structure is formed which makes them more elastic than the ceramic-bonded bricks. Addition of 5–20% flake graphite increases heat transfer, lowers thermal expansion and attack by the slag, and improves thermal shock resistance. This development is applied in electric arc furnaces, converters, and metal ladles for secondary steelmaking processes. The low-oxygen atmosphere formed in these bricks during use can cause significant reduction of the magnesite. To prevent this, manufacturers have recently developed high-quality magnesite with larger periclase crystals and a low internal sinter surface area [120].

Chemically bonded bricks with chrome ore contain chemical bonding agents (e.g., Epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and are produced in the same way as fired magnesite bricks up until the drying stage. The bonding agents decompose and form a ceramic when the bricks are used at high temperature.

Pig iron mixers, transport vessels, and secondary refining ladles used in the steel industry are lined with magnesite bricks. Sliding

gates and nozzles are also made from sintered magnesite.

On account of their high refractoriness (refractoriness under load and low creep in compression), resistance to alkali, and high heat storage capacity, magnesite bricks are used in the crowns, port linings, and the hot parts of the checkerwork in glass-melting tanks. Magnesite chrome or magnesite spinel bricks are more suitable for the sintering zones of rotary cement kilns due to their good stress deformation behavior. Magnesite bricks are preferred for lime shaft kilns. Large quantities of sintered magnesite are used for unshaped repair materials.

The increased demands made on refractory materials as a result of higher operating temperatures and shorter tap to tap times in metallurgical furnaces and reactors can only be met by pure, high-density magnesite sinters. Small quantities of “contaminants” are disadvantageous if they form low-melting eutectics with MgO (e.g., with CMS at 1485 °C or with C_2F at 1200 °C, Table 20.11) because this leads to deterioration of mechanical properties (e.g., strength and volume stability) at high temperatures. High-quality sinters therefore have a low content of high-melting silicate phases (such as C_2S), a low B_2O_3 content, and a high degree of direct periclase-periclase contact (without intermediate silicate phases).

Use of Sintered Magnesite as a Heat-Storage Medium

Magnesite bricks have a high heat storage capacity (about 160% that of chamotte) and a high thermal conductivity [121]. They are used in efficient off-peak storage heaters. The heat generated by a heating element is transferred to the magnesite brick and increases its temperature.

The most suitable bricks are fired and have the following properties: a high bulk density (up to 3.10 g/cm³) and thus a high degree of sintering, a high thermal conductivity (up to 9 Wm⁻¹K⁻¹ at 600 °C), and a high specific heat (1.1 kJkg⁻¹K⁻¹ at 600 °C). The influence of

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impurities on these factors is not as critical as in refractories.

The bulk density depends on the chemical composition, the sinter porosity and the method used to produce the bricks. Thermal conductivity is increased by a high periclase content and a low porosity. The specific heat is only slightly lowered by SiO_2 and Al_2O_3 , but is significantly lowered by CaO , Cr_2O_3 , and Fe_2O_3 . The bricks should not contain free CaO (risk of hydration) or crystal phases with different modifications.

Uses of Caustic Magnesia

Agriculture. In the 1970s and 1980s the use of caustic magnesia increased the most in fertilizers and animal feeds [122–125]. Magnesium is a constituent of plant-chlorophyll and also plays a role in enzyme activity. It is regarded as an essential plant nutrient and is used in fertilizers. Magnesium deficiency (symptoms: chlorosis, necrosis) became especially common after fertilizers containing a high percentage of potassium replaced potassium–magnesium fertilizers based on kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$). In countries with salt deposits (e.g., Germany), magnesium is supplied in the form of kieserite, magnesia lime ($> 10\%$ MgO), and calcined dolomite. In all other countries (e.g., Netherlands, UK, USA), caustic magnesia (particle size 4 mm, $\geq 70\%$ MgO) and magnesite are used.

Ground caustic magnesia (particle size ≤ 2 mm, $\geq 85\%$ MgO) is used as a supplement for animal feeds. Magnesium is usually present in green fodder, but cattle and sheep feeding on fodder from slightly acid soils may suffer from “grass staggers” in spring which is caused by magnesium deficiency.

Building Industry. Caustic magnesia mixed with concentrated solutions of magnesium salts and a small amount of sodium phosphate becomes extremely hard and sets in air (e.g., with MgCl_2 solutions it forms $3\text{MgO} \cdot \text{MgCl}_2 \cdot 11\text{H}_2\text{O}$). However, the hardened material is not stable in water and is therefore not a true cement (which must set in air and water) but a

magnesia binder. These binders were originally referred to as Sorel cement or as stone-wood (xylolith) when mixed with sawdust as a filler. Since their high chloride content can corrode metals and other construction materials, magnesia binders must never be reinforced. They can be used as mastics or protective coatings at room temperature. Large quantities of caustic magnesia derived from carbonate are used for stonewood or plaster flooring in the Eastern Bloc. The low-iron caustic magnesia generally used for this purpose contains 75–87% MgO and is ground ($40\text{--}45\% < 10 \mu\text{m}$).

An important use of caustic magnesia is in *lightweight construction boards* (Heraklith) for thermal and acoustic insulation (thickness 5–100 μm). The boards are produced on fully automatic lines at ca. 60 °C from finely ground caustic magnesia (MgO content 65–80%, starting material magnesite containing silicates and dolomite), MgSO_4 solution as a binder, and impregnated pinewood chips. Mineral wool is also used as a filler. Subsequent hardening results in highly nonflammable boards which can be made fire-retardant and resistant to moisture and microorganisms by coating one side with plaster. The prefabricated boards are used to make formworks for concrete, and large quantities are used in combination with polystyrene in laminated boards.

Other Uses. Caustic magnesia containing ca. 70–99% MgO is used in wastewater treatment in prevention of corrosion, as a buffer, in preparative chemistry, and in the pharmaceutical industry.

Caustic magnesia can be used to remove heavy metals and silicate from wastewater. Ammonia can be precipitated and removed in the form of $\text{Mg} \cdot \text{NH}_4 \cdot \text{PO}_4 \cdot 6\text{H}_2\text{O}$ following addition of phosphoric acid and caustic magnesia [126]. The magnesium ammonium phosphate can be used as a fertilizer. This principle is also used to remove phosphate. Caustic magnesia is a mild base and neutralizes acids and acidic water, it also acts as a weak buffer.

Low-iron caustic magnesia is used as a filler in the plastics and rubber industries and

allows adjustment of viscosity and stiffness. It also acts as a chlorine acceptor in chlorinated hydrocarbon polymers and stabilizes them.

Large quantities of pure magnesium oxide are used in the chemical industry for the synthesis of magnesium compounds. Basic magnesium sulfonates and finely dispersed MgO are used as lubricant and motor fuel additives to neutralize combustion residues. Magnesium oxide in fuels binds sulfur and other compounds and prevents formation of acidic exhaust gases.

Large quantities of caustic magnesia are used in the paper and cellulose industries (magnesium bisulfite digestion). Caustic magnesia with graded particle size is also used as a polishing agent.

Caustic magnesia, magnesium carbonate (precipitated from caustic magnesia), and high-purity magnesia are utilized in preparative chemistry and cosmetics. In the pharmaceutical industry magnesium oxide ($\geq 98\%$ MgO) is used as an antacid, as a powder base, and for magnesium substitution therapy.

A potential use of caustic magnesia is as a slag additive to reduce the dissolution of MgO from refractory bricks in the steel industry. Treatment of the surface of grain-oriented steel transformer sheets decreases magnetic losses. A suspension of caustic magnesia is applied to the sheet and annealed.

Uses of Magnesium Hydroxide

The most important use of magnesium hydroxide is as an intermediate in the production of magnesia. In Japan it is used to replace polyhalogenated diphenyl ether as a flame retardant in thermoplasts processed at 200–350 °C. Hydrated alumina cannot be used at these temperatures because of its low decomposition temperature. This application is being tested in Germany [127]. Well-dispersed single $\text{Mg}(\text{OH})_2$ crystals seem to be more suitable than agglomerates.

Table 20.15: Production capacities for sintered and caustic magnesia in 1988/1989 (10^6 t/a) [108].

Country	Sintered magnesia		Caustic magnesia	
	Natural magnesite	Seawater and brines	Natural magnesite	Seawater and brines
EEC	0.6	0.5	0.3	0.1
Western Europe (not EEC) and Asia Minor	0.9	0.14	0.2	< 0.1
Eastern Bloc	2.8			
North and South America	0.4	0.7	0.2	> 0.1
Asia	2.0	0.6	0.3	< 0.1
Australia	« 0.1		« 0.1	
Africa	« 0.1		« 0.1	
World total	6.8	1.9	1.0	0.4

20.11.3.4 Economic Aspects

Developments in the production capacities, production, and consumption of magnesia can be briefly summarized as:

- 1974 World magnesia shortage [128]
- 1977 From shortage to surplus [129]
- 1981 Agricultural oversupply and industrial underdemand for caustic magnesia [123]
- 1982 Contraction of refractory magnesia and stagnation of caustic magnesia [130]
- 1984 China, the magnesite giant [131]
- 1987 The world magnesia industry, smaller but fitter and purer [132]
- 1989 Magnesia markets – fit for optimism [108]

These changes reflect the dependence of economics on the economic and technological developments in the steel industry. The discovery of highly pure magnesite deposits in Australia in 1985, which will allow magnesia to be obtained directly from the carbonate, has led not only to optimism for producers there, but also to concern among those using the energy-intensive process via magnesium hydroxide.

Recent developments are aimed at reducing energy consumption by improving the filterability of precipitated products, optimizing kiln design, and increasing the size of the periclase crystallites and the bulk density of sintered magnesia. The estimated production capacities for caustic and sintered magnesia are given in Table 20.15. The estimated production of crude magnesite ore increased from $16 \times 10^6 \text{ t/a}$ in 1981 to $20 \times 10^6 \text{ t/a}$ in 1988.

20.11.3.5 Fused Magnesium Oxide

Properties

Fused magnesia is crystalline magnesium oxide (*mp* 2800 °C) that has been melted in an electric arc. It has the same crystal structure as sodium chloride (i.e., face-centered cubic) and occurs naturally as periclase. No phase changes take place on heating up to the melting point.

Pure fused magnesia is white, although the presence of iron impurities impart a greenish color due to the presence of the mixed crystal compound magnesio-wüstite (Mg,Fe)O. When the pale green fused magnesia is heated in air, the color changes to brown owing to the formation of magnesioferrite (MgFe₂O₄) [134].

Fused magnesium oxide has a much lower tendency to undergo hydration than sintered magnesium oxide or caustic calcined magnesite [135], and is essentially stable towards the atmosphere. Thus, polished crystal faces of periclase only begin to lose their luster after several weeks, depending on atmospheric moisture content and temperature. Reaction with atmospheric carbon dioxide to form basic carbonates is also noticeable only after several weeks or months. Fused magnesia is stable in an oxidizing atmosphere up to ca 2200 °C, above which vaporization and partial dissociation take place. Theoretical vapor pressures of magnesium oxide and partial pressures of its dissociation products in the temperature range 1227–2727 °C are given in [136].

In a reducing atmosphere (e.g., in the presence of carbon), fused magnesia is stable only up to ca 1700 °C. This temperature is also the limit for vacuum use because of the resultant vapor pressure [137].

The most important physical properties of fused magnesia (e.g., thermal conductivity and electrical resistivity) depend on the density, purity, particle size distribution, type, and distribution of the foreign mineralogical phases present. Consequently, data obtained from measurements on single magnesium oxide crystals [138] or pure, polycrystalline magnesium oxide (> 99%) cannot be regarded

as characteristic of commercial fused magnesia.

The following data (see also Section 20.11.3.1) are therefore partly based on information from manufacturers of fused magnesia and include the grades most commonly available today (MgO content > 92%, particle size 0–400 µm):

Density of pure periclase (theoretical)	3.56–3.58 g/cm ³
Knoop hardness	370
Mohs hardness	6
Linear thermal expansion coefficient (1000 °C)	14 × 10 ⁻⁶ K ⁻¹
Specific heat (<i>c_p</i>)	
100 °C	0.96 kJ/kg·K ⁻¹
1800 °C	1.21
Thermal conductivity (1000 °C) for densities of 3.0–3.58 g/cm ³	ca. 2.9–8.4 Wm ⁻¹ K ⁻¹
Dielectric constant, ϵ (30 Hz–1 MHz)	11
Electrical resistivity (technical grades, manufacturers' data)	
600 °C	2 × 10 ⁹ –10 ¹¹ Ω·cm
800 °C	3 × 10 ⁸ –2 × 10 ⁹
1000 °C	10 ⁷ –9 × 10 ⁷
Electrical resistivity of MgO single crystals (for comparison)	
500 °C	2 × 10 ¹³ Ω·cm
1000 °C	6 × 10 ⁸

Production

Fused magnesia is mainly produced from naturally occurring magnesite (MgCO₃) that has been calcined at 1200–1400 °C ("dead burned"). The calcined product usually contains > 92% MgO, 1–4% SiO₂, 0.5–2% CaO, 0.1–2% Al₂O₃, up to 0.2% Fe₂O₃, and traces of ZrO₂, NiO, Na₂O, K₂O, B₂O₃, and S. Magnesite from seawater, containing > 97% MgO, is also used as a raw material.

When fused magnesia is used as an electrical insulator for heating applications (tubular elements), the amount of conductive impurities in the raw material must be minimal. Therefore magnesites that contain, for example, iron oxides or sulfur in appreciable amounts cannot be used. Contamination with sulfur is avoided by calcining the magnesite in wood-fired furnaces.

Fused magnesia is usually produced in a batch process by melting the raw material at 2800–3000 °C in electric arc furnaces [139].

The furnaces are heated by either single-phase or, more usually, three-phase a.c. current (Higgins furnace, block-making process). They have a moving base and a conical, water-cooled steel cover. The raw material is added batchwise and acts as a refractory lining for the furnace walls, and the furnace base is usually lined with magnesite bricks or a rammed graphitic material bonded with bitumen. The furnaces are heated by either two or three graphite electrodes. The arcs are struck onto a layer of coke and the electrodes can be vertically adjusted to suit the height of the molten bath.

The current in, for example, a 1000-kW a.c. electric arc furnace (Higgins furnace) is 6000–9000 A at 90–150 V. The electric power required to produce the fused blocks is ca. 2000–4000 kWh/t [139].

In addition to the traditional block-making process (Higgins furnace), tilting furnace technology is also used for the industrial production of fused magnesia [140]. The melting process is continuous, and the molten product is poured intermittently into water-cooled or refractory-lined molds. Manufacture of fused magnesia by an electric arc trough melting process [141] and in a high-frequency plasma [142] has also been described.

On completion of melting, the electrodes are withdrawn and, after a cooling period, the furnace cover is removed. The fused magnesia blocks can weigh as much as 20 t. After cooling to room temperature, preliminary size reduction is carried out. This is followed by further size reduction of the large broken pieces. The blocks are not homogeneous with respect to structure or chemical composition, and their surface is covered with a coating or crust of agglomerated sintered magnesia.

The impurities in the raw product consist of compounds formed from the quaternary system MgO–CaO–SiO₂–Fe₂O₃, e.g., magnesium silicates such as forsterite (2MgO·SiO₂, *mp* 1890 °C) and monticellite (CaO·MgO·SiO₂, *mp* 1500 °C, incongruent melting) whose melting points lie far below that of pure magnesium oxide. The foreign phases are mainly concentrated locally in the surface zone of the

fused block and constitute the "melt residues" along with imperfectly melted magnesium oxide (the sintered crust). They are hand separated from the fused product which is a white to pale green crystalline periclase with crystallite sizes from several hundred micrometers up to several centimeters. Hand sorting is the normal industrial method of impurity removal, no better method has yet been found. However, some of the silicate impurities associated with the raw material form inclusions of foreign phases in the crystals of the pulverized magnesium oxide end product. This is because the rate of growth of the magnesium oxide crystals in certain regions of the solidifying melt is greater than the migration rate of the melt residues. Thus, magnesium oxide blocks from a Higgins furnace contain foreign phases (monticellite and forsterite) deposited at the grain boundaries, while magnesium oxide produced by casting from a tilting furnace usually exhibits an intracrystalline distribution of these phases (Figure 20.23). Further treatment of the hand-sorted, size-reduced, fused product includes several size reductions with jaw crushers, roller crushers, and gyratory crushers. Iron particles produced by abrasion and other magnetic impurities are removed by high power magnetic separators. Finally, the finely grained material is classified into particle size ranges using a series of sieves. Fused magnesia intended for electrical heating applications is heated in an oxidizing, neutral, or reducing (although not carbon-forming) atmosphere at 1100–1400 °C [143] to remove moisture and carbon (originating from breakdown of the electrodes) and to reduce surface and lattice defects of the magnesium oxide particles.

Uses

Fused magnesia is mainly used as an *insulating material* in the electrical heating industry. The particulate material is packed into the space between the heating coil and the outer tube in a heating element for air or liquids [144]. Such elements are used in IR heaters, grill elements, tubular hot plates, and tubular

heating elements for ovens, storage heaters, radiators, continuous-flow heaters, washing machines, coffee machines, electric irons, and industrial liquid heating equipment.

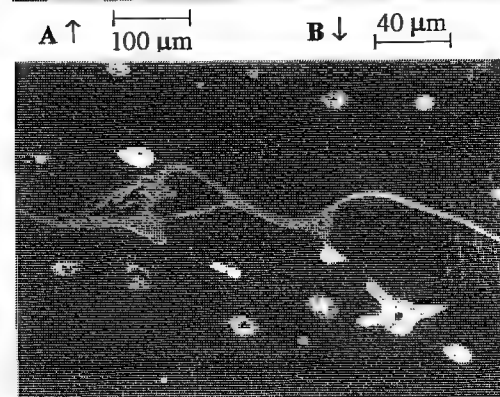
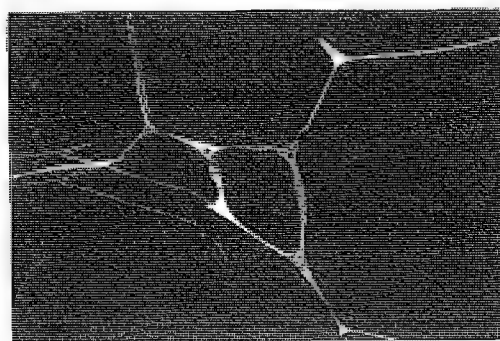


Figure 20.23: Photomicrograph of polished sections of fused magnesite (dark areas: MgO; light areas: foreign phases monticellite and forsterite). A) Magnesite produced in a Higgins furnace: foreign phases deposited at the grain boundaries; B) Magnesite produced by casting in a tilting furnace: foreign phases occur mainly as intracrystalline material.

The most important factor in this application of fused magnesite is its combination of high electrical resistance with high thermal conductivity. This is superior to that of other refractory oxides or other materials.

The grade of magnesium oxide recommended depends on the application for which the heating element is used (surface temperature of the tube) and the electrical insulation requirements. The grades usually have a size range of 0–400 μm and a tap density of 2.2–2.7 g/cm³. The product must have well-defined flow properties, which can be influenced

by modifying the particle shape by treatment in a fluidized bed [145].

The electrical and thermal properties of fused magnesite can be improved by adding synthetic or natural minerals (e.g., pyrophyllites [146], fused zircon sand [147], enstatite [148], cordierite [149], or magnesium aluminum silicates [150]) to the prepared mixture of magnesite particles. The mechanism of action of these additives has not yet been explained.

The chemical composition of some of the industrial grades of fused magnesite (electrical grade) are given in Table 20.16. The important properties of the mixture of fused magnesite particles (as used for electrical heating, i.e., thermal conductivity, long life time, sinter index, specific electrical impedance, leakage current, tap density, flow rate, grain size distribution) are tested by standard methods (ASTM D2858, D2900, D3026, D3215, D3347; DIN 44872).

Fused magnesite has a further application as a *refractory material*, especially as a lining for induction furnaces and crucibles. Induction furnace linings based on fused magnesite do not shrink (unlike those based on sintered magnesite) owing to the low porosity of the fused material. Magnesite graphite bricks with an addition of fused magnesite [151] are used in ultrahigh-power furnaces for steel production. The low porosity of the fused magnesite and the size of the periclase crystals considerably improve the corrosion resistance of the refractory lining. The refractory-grade material has a lower SiO₂ content and a higher CaO:SiO₂ ratio than the electrical-grade fused magnesite (i.e., for electrical heating, see Table 20.16). In special applications, fused magnesite is also used as a molding material for precision casting, as a raw material for magnesium oxide ceramics and as single crystals [152] for optical windows and lenses.

Economic Aspects

The most important countries and companies producing fused magnesite are:

France	Pechiney Électrometallurgie
Germany	Hüls AG

Table 20.16: Chemical composition (typical) of some commercially available fused magnesite grades.

Producer	Grade	MgO, %	SiO ₂ , %	CaO, %	Fe ₂ O ₃ , %	CaO:SiO ₂ ratio	Density, g/cm ³
Pechiney, France	Ca 250 ^a	95.5 (min.)	2.2	1.5	0.008	0.68	2.39 ^b
Hüls, Germany	Dynatherm ^a 1246 CS	96.3	2.0	1.5	0.10 (max.)	0.75	2.36–2.40 ^b
Thermal Syndicate, UK	Maglox ^a 1GN1	96.8	2.3	0.8	0.10	0.35	2.35–2.40 ^b
Universal Abrasives, UK	M 70 ^a	93.1	3.7	1.6	0.16	0.43	2.36–2.40 ^b
Muscle Shoals Minerals, USA	22SR ^a	96.0	3.1	0.8	0.07	0.26	2.38–2.41 ^b
Pechiney, France	UR1 AT ^c	98.0	0.5	1.1	0.15	2.2	2.50 ^d
Baymag, Canada	Electromag ^c	96.7	0.2	2.2	0.5	11	3.50 ^d
Tateho, Japan	KMA ^c	98.5	0.35	0.9	0.15	2.6	3.57 ^d

^aElectrical grades for high-duty tubular heating elements.

^bTap density according to ASTM D3347, grain size 40–325 mesh.

^cRefractory grades.

^dApparent density.

United Kingdom	Universal Abrasives, Thermal Syndicate
Austria	Österreichisch Amerikanische Magnesit AG (refractory grades)
United States	Muscle Shoals Minerals, Tateho America (formerly CE-Minerals), Insultherm
Canada	Baymag (refractory grades)
Japan	Tateho Chemical Ind.

Further information on these manufacturers (e.g., production capacities) is given in [153].

The world consumption of fused magnesite for electrical heating (electrical grade) is estimated to be ca. 35 000–40 000 t/a. There are no figures available for refractory grade material because the grades of fused magnesite are not listed separately in the statistics.

20.11.4 Magnesium Sulfate

Magnesium sulfate does not occur in nature in anhydrous form. It is found in the form of hydrates and double salts in salt and potash deposits (e.g., in the United States, Germany, and the former Soviet Union). Magnesium sulfate also occurs in dissolved form in salt lakes.

20.11.4.1 Properties

The transformation temperatures of the stable magnesium sulfate hydrates and their solubilities in water are given in Table 20.17. Table 20.18 lists the molecular masses, the specific heats, refractive indices, and crystal classes of the anhydrous salt and some of the hydrates [154, 155]. Anhydrous magnesium sulfate can be obtained without decomposition

by dehydrating the hydrates at 400–500 °C. At 700 °C, however, the compound decomposes to give magnesium oxide, sulfur dioxide, and oxygen. This accounts for the fact that the melting point of magnesium sulfate cannot be accurately determined, it is between 1120 and 1150 °C.

Table 20.17: Stable magnesium sulfate hydrates.

Hydrates	Transformation temperature, °C	Solubility, g MgSO ₄ /100 g H ₂ O
Ice–MgSO ₄ ·12H ₂ O	–3.9	22.0
MgSO ₄ ·12H ₂ O–MgSO ₄ ·7H ₂ O	1.8	27.2
MgSO ₄ ·7H ₂ O–MgSO ₄ ·6H ₂ O	48.1	49.5
MgSO ₄ ·6H ₂ O–MgSO ₄ ·H ₂ O	67.5	56.6

Table 20.18: Properties of magnesium sulfate and its hydrates.

Compound	Specific heat, kJ kg ^{–1} K ^{–1}	Density, g/cm ³	Crystal class	Refractive index
MgSO ₄	0.800	2.66	orthorhombic	
MgSO ₄ ·H ₂ O	1.047	2.57	monoclinic	1.523, 1.535, 1.586
MgSO ₄ ·2H ₂ O	1.124			
MgSO ₄ ·4H ₂ O	1.305	2.01	monoclinic	1.490, 1.491, 1.497
MgSO ₄ ·6H ₂ O	1.525	1.75		1.456, 1.453, 1.426
MgSO ₄ ·7H ₂ O	1.546	1.68	orthorhombic	1.432, 4.4554, 1.4609

Magnesium sulfate is hygroscopic and absorbs water to form hydrates, finally the heptahydrate. Various hydrates can be obtained by

stepwise dehydration of higher hydrates or by crystallization from aqueous solution. Hydrates of analogous composition can be produced by these two methods, but X-ray crystallography shows that their structures differ due to destruction of the crystal lattice during dehydration.

Five stable hydrates can be crystallized from aqueous solutions: $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salt, epsomite, Bittersalz), $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (hexahydrate), $\text{MgSO}_4 \cdot \frac{5}{4}\text{H}_2\text{O}$ ($\frac{5}{4}$ hydrate or synthetic kieserite) and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (kieserite). Three metastable forms also occur: a second form of the heptahydrate, $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ (allenite), and $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ (leonardite). Stepwise dehydration yields hydrates with 1, $\frac{5}{4}$, 2, 3, 4, and 6 molecules of water. The solubility of kieserite decreases with increasing temperature due to its negative heat of dissolution. Its dissolution rate increases with increasing temperature and decreasing pH.

The acid sulfates $\text{MgSO}_4 \cdot \text{H}_2\text{SO}_4$ and $\text{MgSO}_4 \cdot 3\text{H}_2\text{SO}_4$ crystallize when MgSO_4 is dissolved in sulfuric acid. Magnesium sulfate-ammine hydrates ($\text{MgSO}_4 \cdot 3\text{NH}_3 \cdot 3\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 2\text{NH}_3 \cdot 4\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$) are produced when Epsom salt reacts with gaseous ammonia. On reaction with alkali, magnesium hydroxide precipitates out; a precipitate of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) is formed with sodium carbonate. After addition of sulfite, phosphate, or stearate solutions, insoluble magnesium sulfite, magnesium phosphate, or magnesium stearate precipitates out. Magnesium chloride reacts with magnesium oxide to form oxychlorides, magnesium sulfate reacts in the same way to form oxysulfates ($\text{MgSO}_4 \cdot 3\text{MgO} \cdot 11\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 5\text{MgO} \cdot 8\text{H}_2\text{O}$): it can therefore be used as a slower type of sulfate Sorel cement binder. Magnesium sulfate forms double salts with other salts, most of which also occur in nature:

$\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ kainite

$\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$ langbeinite

$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ leonite

$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ schönite (picromerite)

$\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ astrakanite (bloedite)

$6\text{Na}_2\text{SO}_4 \cdot 7\text{MgSO}_4 \cdot 15\text{H}_2\text{O}$ loewite

$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ polyhalite

20.11.4.2 Occurrence and Raw Materials

The most important source of MgSO_4 in Germany is kieserite, which is a constituent of raw potash salt. In the United States, MgSO_4 is obtained from langbeinite and in Italy from kainite. The raw salts used by the potash industry in the former Soviet Union (Stebnik, Kalush) contain magnesium sulfate salts. Magnesium sulfate is also found in the brines of the Great Salt Lake and the Kara-Bogaz Gulf of the Caspian Sea. Seawater bitterns provide a further source (Epsom salt), the MgSO_4 is obtained by cooling. In many countries MgSO_4 is also produced from magnesite, dolomite, seawater magnesia, or other magnesium minerals.

20.11.4.3 Production

Production of Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$)

Production of Kieserite by Selective Dissolution of Residues from Potash Salt Production. The raw material for this process is a crude salt that contains kieserite (hard salt, carnallite). The sodium chloride is selectively dissolved from residues of potash salt production. The filtered or centrifuged residues obtained during the production of potassium chloride are first washed with a partially saturated NaCl solution from a subsequent washing step. The NaCl in the residues is readily soluble and dissolves in the NaCl solution until it becomes saturated; the kieserite, however, remains largely undissolved due to its slow dissolution rate. Kieserite and residual NaCl are separated from the washing medium with a bucket conveyor or elevator. The kieserite-NaCl mixture is then washed with water in a second stage to dissolve any residual NaCl. Washing is performed in pipes lined with fused basalt that are several hundred meters long. The quantity of NaCl solution

produced can be minimized by using the electrostatic production process (see below).

Ecological Aspects. The saturated NaCl solution contains 280–300 g NaCl per liter. Its disposal entails considerable ecological problems. Large quantities have been stored in jointed rock formations (platy dolomite) that are filled with slightly salted groundwater, but with only limited capacity [156].

Production of Kieserite by Flotation. Kieserite can be separated from rock salt by flotation. Prestaminol, oleic acid, fatty alcohol sulfates, or oxystearic acid are used as flotation agents for kieserite and anhydrite (CaSO_4) [157]. The kieserite can be further purified by separating it from the anhydrite and/or langbeinite. This is achieved by using oleic acid or a fatty acid amine as a flotation agent for the kieserite [158–160].

Electrostatic Separation of Kieserite. The electrostatic production process (ESTA process) developed by Kali und Salz AG (Germany) eliminates the formation of the large quantities of NaCl solution produced in the selective dissolution process (see above) [161, 162].

Kieserite can be electrostatically separated in one or two stages. In the one-stage process the raw salt is treated with aliphatic or a mixture of aliphatic and aromatic monocarboxylic acids that are combined with ammonium salts of aliphatic carboxylic acids, usually ammonium acetate. The salt is then heated at a defined relative humidity and electrostatically charged [163]. The kieserite becomes positively charged with respect to the potassium chloride and sodium chloride. Repeated separation of the kieserite deposited at the negative electrode yields MgSO_4 in an extremely pure, marketable form.

In the two-stage process rock salt is first separated and then the highly pure kieserite. The raw salt is first treated with aromatic monocarboxylic acids, heated at a defined relative humidity, and then charged [164]. The rock salt becomes positively charged with respect to the potassium chloride and the

kieserite. The rock salt is removed and the KCl-kieserite mixture separated at the positive electrode. The mixture is treated with aliphatic monocarboxylic acids, heated once again at a defined relative humidity, and charged [163]. The kieserite now becomes positive with respect to the potassium chloride. Repeated separation of the kieserite deposited at the negative electrode gives an extremely pure, marketable product.

The potassium chloride fraction is still contaminated with kieserite and sodium chloride; it is used for the production of potassium salts [165, 166].

Production of Granulated Kieserite. After addition of 3 parts of a solution containing preferably 18% Na_2SO_4 or 20% Na_2PO_4 to 47 parts of kieserite, the product can be pressed in a moist state and then ground [167]. After addition of ammonium sulfate and hot magnesium sulfate solution, kieserite can also be granulated with a dish granulator [168]. Mono-, di-, or polysaccharides (usually lactose) are highly suitable additives for preparing these rolled granulates. The kieserite should have a broad particle size range; at least 20% of the particles must be less than 0.09 mm in diameter [169]. Addition of phosphate allows production of a rolled granulate of high strength even without drying [170].

Production of Epsom Salt

Production of Epsom Salt from Kieserite. Kieserite is dissolved in hot water (90 °C) to give a clear solution. Dissolution is performed in single large vats with capacities of up to 500 m³ that have a sieve base covered with coconut mats. The process has the disadvantage that the throughput is very low and the sieve plate gradually becomes encrusted with anhydrite and double salts. Kali und Salz AG therefore uses a multichamber cascade with slow stirring; the slurry density in the chambers is 70%. Hot water is added from below and kieserite from above. The solution produced at the top of the cascade contains 400 g/L

MgSO₄. At the bottom the residue containing anhydrite can be removed at intervals [171].

The hot concentrated solution is cooled in multistage vacuum coolers in which large crystals of Epsom salt are formed. After thickening, the Epsom salt is either filtered or centrifuged. The moist salt is dried in drum driers with air at ca. 50 °C.

Production of Epsom Salt from Magnesite, Magnesite, and Other Materials. Magnesium sulfate solution can be produced by treating seawater magnesite (MgO) or magnesite (MgCO₃) with sulfuric acid. Waste sulfuric acid contaminated with organic compounds may be used [172]. The resulting solution is clarified, evaporated to a density of 1.35–1.36 kg/L, and processed as described above. The product can be spray dried at 150 °C. Dolomite, olivine, serpentine, or peridotite can also be reacted with sulfuric acid. Magnesium sulfate can also be obtained by adding MgO to pyrite during roasting and subsequent extraction [173].

Waste serpentine from asbestos production can be reacted with ammonium sulfate above 250 °C and the reaction mixture extracted with water [174, 175]. The resulting solution is evaporated and the Epsom salt crystallizes out.

Production of Epsom Salt from Seawater Bitterns or Salt Lakes Brines. Pure Epsom salt can be obtained directly from seawater bitterns and from brines from salt lakes with a high MgSO₄ content (e.g., Kara-Bogaz Bay) by diluting with water and cooling to –10 °C [176, 177].

Production of Epsom Salt from Langbeinite. Langbeinite (K₂SO₄·2MgSO₄) is decomposed by treating with water for 6 h at 50–60 °C to produce MgSO₄·6H₂O. On cooling the mother liquor to 20–35 °C the Epsom salt crystallizes out [178].

Production of Epsom Salt from Magnesite or Dolomite and Gypsum. A mixture of ground dolomite and gypsum is treated with steam at 1.5–3.0 MPa and filtered to remove

the CaCO₃ from the MgSO₄ solution [179]. Magnesite is calcined at 760–835 °C, hydrated in the presence of gypsum at 56–60 °C, and carbonized with carbon dioxide. The MgSO₄ solution is filtered to remove the CaCO₃ [180] and processed to obtain Epsom salt.

Production of Anhydrous Magnesium Sulfate

Anhydrous MgSO₄ does not occur in nature and can only be produced by dehydrating MgSO₄ hydrates. Kieserite is purified by removing anhydrite and langbeinite in a special electrostatic procedure. It is subsequently washed with water to remove residual chloride [181]; langbeinite and anhydrite may also be removed by flotation. It is then dehydrated by heating at ca. 500 °C in a gas-heated calcination drum and finally cooled [182]. If Epsom salt is used as starting material instead of kieserite, six molecules of water of crystallization can be removed at < 70 °C and the remaining molecule at 500 °C.

20.11.4.4 Quality Specifications and Analysis

Magnesium sulfate is sold as kieserite (73–83% MgSO₄), 99.9%-pure Epsom salt (48.8% MgSO₄), and anhydrous MgSO₄ (> 98% MgSO₄). Epsom salt is marketed as a chemically pure product, as a clinical product that complies with pharmacopeia specifications, and as an analytical grade reagent. Maximum contamination limits for clinical grades vary according to the pharmacopeia: chloride 100–300 mg/kg, iron 20 mg/kg, and heavy metals 10 mg/kg. Maximum limits for arsenic, selenium, and other substances may also be specified.

The analytical procedures used for quality control are the same as those employed for magnesium chloride. Sulfate, however, is determined by a gravimetric method [183].

20.11.4.5 Transportation and Storage

Depending on the atmospheric humidity, Epsom salt can lose or absorb water during storage and thus tends to harden. It is therefore preferably supplied in Clupack valve sacks. Kieserite is transported in railroad cars and trucks, both in bulk and in valve paper sacks. Anhydrous MgSO₄ is also supplied in bulk and in sacks.

20.11.4.6 Uses

Large quantities of kieserite and Epsom salt are used in Germany for the production of potassium sulfate. Kieserite is used in fertilizers, either as an additive in multinutrient fertilizers or directly to combat magnesium deficiency. In multinutrient fertilizers kieserite aids granulation and improves granulate properties. In cases of acute magnesium deficiency, Epsom salt is an especially effective foliar fertilizer.

Magnesium sulfate is a component of magnesium binders (Sorel cement) and can also be used as a binding agent in the production of magnesite bricks. Addition of MgSO₄ and Al₂(SO₄)₃ leads to the formation of spinels during firing of refractory products. Decomposition of MgSO₄ in refractory products at > 1100 °C results in the formation of sulfur dioxide and thus gives a light product. Magnesium sulfate is also used in the production of Portland cement from blast furnace slag and as an additive in gypsum-containing building materials.

Magnesium sulfate is employed in the sugar industry for refining the sugar liquor and for improving the sugar yield from molasses (Quentin procedure) [184]. It is utilized in fermentations for the production of amino acids, antibiotics, bakers' yeast, biomass, and citric acid. It increases the activity of glucose isomerase, the enzyme which converts glucose to fructose.

In the aluminum industry, a mixture of kieserite and calcium oxide or hydroxide is used to precipitate contaminants from alumi-

nate solutions. Magnesium sulfate is also employed in fixative baths used to color aluminum surfaces by means of anodic oxidation. It is a component of the electrolytic baths used for chrome plating, zinc plating, copper plating, nickel plating, and the electroplating of tungsten, manganese, vanadium, cobalt, and cobalt alloys. It is also used in the phosphating of iron.

In the glass industry, sinters with a defined porosity can be obtained by incorporating MgSO₄ of a defined particle size and then leaching it. Magnesium sulfate is used as an additive in enamels and pigments. In the detergent industry it prevents gel formation during spray drying; magnesium silicate synthesized from MgSO₄ stabilizes peroxides and thus improves bleaching. Magnesium sulfate is also used as a make-up chemical in the sulfite pulping process and as a stabilizer for cellulose during oxygen bleaching of pulp. In the paper industry it is used in the preparation of paper for coating and in the deinking of recycled printed paper.

Other uses include treatment of waste and wastewater and soil stabilization. The compound is also used as an additive in drilling fluids, lead acid batteries, oil and coal fuels, ore preparation, "electrolyte" beverages, low-NaCl salt mixtures, cosmetics, bath salts, infusions, photographic developers, dye baths, and animal feeds.

In the plastics industry MgSO₄ is employed as a coagulant, polymerization catalyst, stabilizer, and flame retardant. In the petrochemical industry it is employed together with manganese chloride for cracking petroleum. Use of MgSO₄ in the leather industry makes the leather more supple, increases its weight, and removes calcium carbonate. Magnesium sulfate is also used as a heat storage medium and as a raw material for the production of magnesium aluminate, magnesium aluminosilicate, and other magnesium compounds. One of the important applications of Epsom salt is as a laxative.

20.11.4.7 Economic Aspects

Epsom salt is produced in many countries, the most important being Germany, Japan, and the United States. It is usually consumed in the country in which it is produced. Only Germany and China export the compound. Other commercially available products are kieserite, anhydrous MgSO_4 , and fertilizers containing kieserite (Germany) and langbeinite (USA). Estimated production figures are given in Table 20.19.

20.11.4.8 Toxicology and Occupational Health

Magnesium sulfate and its hydrates are not dangerous to human health when handled in accordance with the appropriate regulations. The LDL_0 (mouse, oral) for MgSO_4 is 5000 mg/kg. Magnesium sulfate is not listed in the EEC directive of May 5th, 1976 concerning the discharge of hazardous substances into water; it is classified as a nonhazardous substance in the EEC directive of June 12th, 1987 (WGK:O).

Table 20.19: Estimated production and consumption of magnesium sulfate products in 1988 (10^3 t).

Product	Production	Consumption in fertilizers	Consumption in other areas
Anhydrous	110	40	70
Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$)	2300	2250	50
Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)	280	180	100
Sulfate of potash magnesia	1000	1000	
Total	3690	3470	220

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21 Aluminum

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21.1 Introduction

Aluminum is the most abundant metallic element in the earth's crust. It is normally found combined with other elements, and occurs rarely, if at all, in its pure state. However elemental aluminum particles have been dis-

covered in lunar soil and small amounts of native aluminum have been reported in Russia and China. Aluminum appears in a wide variety of minerals combined with oxygen, silicon, the alkali and alkaline-earth metals, and fluorine, and as hydroxides, sulfates, and phosphates. Aluminum has become the pre-

dominant nonferrous metal in use, yet it is one of the newest of the common metals. Aluminous minerals are quite stable; large amounts of energy and high temperatures are required to reduce these compounds to metal. This explains why the metal has been isolated and produced commercially only in relatively recent times.

In the late 18th and early 19th centuries many famous scientists worked at isolating aluminum, including LAVOISIER, DALTON, BERZELIUS, DAVY, and ØRSTED. In 1825 HANS CHRISTIAN ØRSTED discovered a method to prepare anhydrous aluminum chloride, a compound that was to play an important role in the production of the metal. ØRSTED is sometimes credited with the discovery of aluminum but often that honor is accorded to FRIEDRICH WÖHLER. His isolation of aluminum in 1827 was based on the reaction in a porcelain crucible of anhydrous aluminum chloride with potassium.

In 1854, H. SAINTE-CLAIRE DEVILLE improved the method of preparing aluminum by substituting sodium for potassium as the reductant for aluminum chloride. He was the first to record that fused cryolite serves as a solvent for aluminum oxide. DEVILLE emerges as the outstanding figure in aluminum technology in the period after its discovery and before commercialization of the Hall-Héroult process. His development of the chemical reduction process raised aluminum from a laboratory curiosity to a useful metal.

The chemical production process was further refined throughout the second half of the 19th century and the aluminum industry grew significantly during this period. Chemical production of aluminum by reduction of cryolite or aluminum fluoride with sodium or potassium was also under development in the late 19th century. The metal exhibited at the Paris Exposition of 1889 was produced at Alliance Aluminium of London, probably by sodiothermic reduction of cryolite. Reduction methods were used into the 1890s, when electrolyte production became dominant.

In the late 19th century many unsuccessful attempts were made to electrolyze aluminum

from aqueous solutions. Aluminum was first prepared electrolytically by a method discovered independently in 1854 by DEVILLE in France and BUNSEN in Germany. A sodium chloride-aluminum chloride fusion was electrolyzed in a porcelain crucible using carbon electrodes. Production based on this electrolysis of aluminum chloride was begun in 1975 by the Aluminum Company of America but operation was abandoned in 1982 for economic reasons.

For a discussion of the Hall-Héroult process, see Section 21.4.1.

21.2 Properties of Pure Aluminum

Certain physical and chemical properties of aluminum depend primarily on purity. There is no generally accepted nomenclature for the degrees of purity of aluminum. The following classification is suggested:

% Aluminum	Designation
< 99.0	Low grade
99.0-99.9	Commercial purity
99.90-99.95	High purity
99.95-99.996	Super purity
> 99.996	Extreme purity

The aluminum produced by the Hall-Héroult process is of commercial purity. Iron and silicon are the predominant impurities. Aluminum of super purity, produced by the three-layer electrolytic process, first became available in 1920 (see Section 21.5). The properties of this grade of metal have been studied extensively. Methods for preparing aluminum of even higher purity include zone refining, fractional crystallization, and preparation from aluminum alkyls. Electrical resistivity at low temperatures is employed as a measure of purity for high purity and super purity aluminum. Newer methods for analysis of trace impurities, including activation analysis, have improved the sensitivity and scope of analyses for very pure materials. Aluminum purer than 99.9999% has been prepared and characterized [14].

Many applications of aluminum and its alloys are based upon its inherent properties of low density, high electrical and thermal conductivities, high reflexivity, and great resistance to corrosion. Pure aluminum is soft and lacks strength, but it can be alloyed with many other elements to increase strength and impart a number of useful properties. Alloys of aluminum are light, strong, and readily formable by many metal-working processes; they can be cast, joined, or machined easily and accept a wide variety of finishes.

21.2.1 Mechanical Properties

Some mechanical properties of aluminum of several purities are given in Table 21.1 [15]. The data are from different sources and caution should be exercised in any direct comparison. Difficulties occur because of problems in analysis, temper of the specimen, and test methods. However, even small amounts of impurities present in commercial aluminum raise the tensile strength and hardness over that of the purest aluminum in the table.

Table 21.1: Mechanical properties of pure aluminum at room temperature.

Purity, %	Tensile strength		Elongation in 50 mm, %
	MPa	ksi ^a	
99.99	45	6.5	50
99.8	60	8.7	45
99.6	70	10.2	43

^a kips (1000 pounds) per square inch.

21.2.2 Physical Properties

The physical properties of pure aluminum are summarized as follows [15]:

mp	660.5 °C
bp	2494 °C
Heat of fusion	397 J/g
Heat of vaporization	10.8 kJ/g
Heat capacity	0.90 J g ⁻¹ K ⁻¹
Density (solid)	
theoretical, based on lattice spacing	2699 kg/m ³
polycrystalline material	2697-2699
Density (liquid)	
at 700 °C	2357 kg/m ³
at 900 °C	2304
Thermal neutron cross section	(2.32 ± 0.03) × 10 ⁻²⁵ cm ² (0.232 ± 0.003 barn)

Lattice constant (length of unit cube) at 25 °C	4.0496 × 10 ⁻¹⁰ m
Coefficient of expansion at 20 °C	23 × 10 ⁻⁶ K ⁻¹
Thermal conductivity at 25 °C	2.37 W cm ⁻¹ K ⁻¹
Volume resistivity	2.655 × 10 ⁻⁸ Ω m
Magnetic susceptibility at 25 °C	16 × 10 ⁻³ mm ³ mol ⁻¹
Surface tension at mp	8.68 × 10 ⁻³ N/cm
Viscosity at mp	0.0012 Pa·s

Atomic Structure, Nuclear Properties [15]. Aluminum has an atomic number of 13 and atomic mass of 26.98154 based on ¹²C. The only abundant isotope, ²⁷Al, is stable and consists of 14 neutrons and 13 protons. Except for a single isotope, ²⁶Al, which has a half-life of 10⁶ years, all isotopes have half-lives of less than 8 s and are of negligible abundance. The naturally occurring isotope has a low cross section for thermal neutrons of 2.3 × 10⁻²⁵ cm², increasing in an irregular manner to 6 × 10⁻²⁵ cm² at 700-800 MeV. The nuclear magnetic moment is 1.84 × 10⁻²⁶ A·m².

Crystal Structure. Aluminum crystallizes in a face-centered cubic lattice that is stable from -269 °C to the melting point. The coordination number is 12 with four atoms to the unit cell. The edge length of the unit lattice cube for pure aluminum is 4.049596 × 10⁻¹⁰ m at 25 °C. Hence, the atomic diameter of aluminum is 2.86 × 10⁻¹⁰ m and its atomic volume 9.999 × 10⁻⁶ m³/mol. The lattice parameter is affected only slightly by impurities.

Thermal Expansion. Values for the coefficient of thermal expansion are given in Table 21.2 [15]. The coefficient of thermal expansion is probably isotropic, meaning it is the same in all directions.

Table 21.2: Thermal expansion coefficient of pure aluminum.

Temperature, K	α (× 10 ⁻⁶ K ⁻¹)	Temperature, K	α (× 10 ⁻⁶ K ⁻¹)
25	0.5	400	24.9
50	3.5	500	26.5
75	8.1	600	28.2
100	12.0	700	30.4
150	17.1	800	33.5
200	20.2	900	37.3
293	23		

Thermal Conductivity. Above 100 K the thermal conductivity of well-annealed 99.99% aluminum is relatively insensitive to

the impurity level. Below 100 K thermal conductivity becomes highly sensitive to the level of impurities. Values for thermal conductivity are given in Table 21.3 [15].

Table 21.3: Thermal conductivity of aluminum.

Temperature, K	Thermal conductivity, Wcm ⁻¹ K ⁻¹	Temperature, K	Thermal conductivity, Wcm ⁻¹ K ⁻¹
<i>Solid</i>		298.2	2.37
0	0	300	2.37
1	41.1	400	2.40
2	81.8	500	2.36
3	121	600	2.31
4	157	700	2.25
5	188	800	2.18
9	239	900	2.10
10	235	933.52	2.08
20	117	<i>Liquid</i>	
30	49.5	933.52	0.907
40	24.0	1000	0.930
50	13.5	1100	0.964
100	3.02	1200	0.994
150	2.48	1300	1.02
200	2.37	1400	1.02
250	2.35	1500	1.07
273.2	2.36		

Electrical Resistivity. The application of aluminum as an electrical conductor depends upon the low electrical resistivity of unalloyed aluminum. The electrical conductivity of pure aluminum at room temperature is 64.94% of that specified for copper in the International Annealed Copper Standard (IACS). At temperatures below 50 K, the electrical resistivity of aluminum is less than that of copper and silver of very high purity. Aluminum becomes superconducting below 1.2 K.

The resistivity of aluminum below 100 K is highly sensitive to purity. The *residual resistivity ratio* (RRR), or the ratio of electrical resistivity at room temperature to that at 4.2 K (boiling point of helium), is sometimes used as a measure of purity. Resistivity ratios of more than 3×10^4 have been reported for 99.999% aluminum.

Values for the electrical resistivity of aluminum are given in tabular form (Table 21.4) and schematically (Figure 21.1).

21.3 Chemical Properties

The 13 electrons in the aluminum atom are distributed: $1s^2 2s^2 2p^6 3s^2 3p^1$. With few excep-

tions the valence of aluminum in chemical compounds is 3+. At elevated temperatures aluminum is monovalent in gaseous molecules, such as AlCl, AlF, and Al₂O. Such species disproportionate at lower temperatures into the normal trivalent condensed compounds and elemental aluminum.

Table 21.4: Electrical resistivity of pure aluminum.

Symbol	Temperature, K	Resistivity, $\mu\Omega \cdot \text{cm}$	Sample
Δ	1.65	9.25×10^{-5}	99.9998% aluminum, single crystal, large diameter (≈ 10 mm)
	4.22	9.25×10^{-5}	
	14	2.61×10^{-4}	
	20.4	7.53×10^{-4}	
	58	8.70×10^{-2}	
	63.5	0.117	
	77.4	0.210	
	90.31	0.351	
	111.6	0.614	
\bullet	273	2.50	99.9% aluminum, 0.05% silicon, 127- μm diameter wire
	373	3.62	
	473	4.78	
	573	6.00	
	673	7.29	
	773	8.63	
	873	10.10	
	923	10.90	
\circ	933	10.95 (s)	99.99% aluminum
	933	24.2 (l)	
	1173	27.75	
	1273	29.2	
	1473	32.15	
---	4.2	5.7×10^{-3}	99.999% aluminum annealed at 150 °C for 4 h
	77	0.22	
	4.2	2.3×10^{-3}	99.9999% aluminum annealed at 150 °C for 4 h
	77	0.22	

21.3.1 Oxidation of Aluminum

Although aluminum is one of the most reactive of the common commercial metals, it is remarkably stable in many oxidizing environments. It owes its stability to the continuous film of aluminum oxide that rapidly grows on a nascent aluminum surface exposed to oxygen, water, or other oxidants. The molecular volume of the oxide is about 1.3 times greater than that of the aluminum consumed in the oxidation reaction. The surface layer, therefore, is under compressive stress and rapidly heals when damaged. In dry oxygen, the surface layer attains a limiting thickness that is a func-

tion of temperature. At room temperature this thickness is about 2.5–3.0 nm.

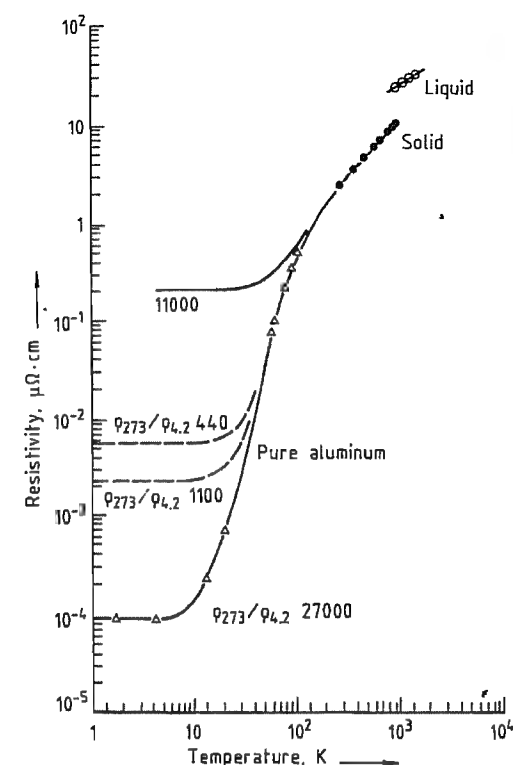
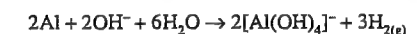


Figure 21.1: Electrical resistivity of aluminum [15].

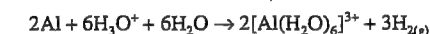
Film thickness is also a function of the amount of water vapor present. At room temperature and 100% relative humidity, about twice as much oxide is formed as in dry oxygen. In both cases, however, the same rate laws apply. Two film layers generally form in wet environments; the continuous oxide layer closest to the metal surface changes to a hydroxylated film at the solid-gas interface. At higher temperatures and on aluminum alloys, especially those containing magnesium and copper, more complex film structures develop, and oxide growth no longer can be described by simple time laws [16].

21.3.2 Reactions with Aqueous Solutions

Large pieces of aluminum of purity greater than 99.95% resist attack by most acids but dissolve in aqua regia. Therefore, aluminum is used to store nitric acid, concentrated sulfuric acid, organic acids, and many other reagents. However, its oxide film dissolves in alkaline solutions; corrosion is rapid, producing soluble alkali-metal aluminate and hydrogen:



Aluminum is amphoteric and can react with mineral acids to form soluble salts and evolve hydrogen:



Molten aluminum can react explosively with water. The mechanism of the reaction is not well understood. Molten aluminum should not be allowed in contact with moist tools or containers.

21.3.3 Reactions at High Temperatures

Molten aluminum reduces many compounds containing oxygen. These reactions are used in the manufacture of certain metals and alloys by the thermite reaction, which is the reaction of a metal oxide with aluminum to produce aluminum oxide (Al₂O₃) and the free metal. Aluminum reduces silicates, particularly glasses. The reaction can start well below the melting point of aluminum.

21.3.4 Corrosion

Atmospheric corrosion is generally electrochemical in nature, depending on current flow between anodic and cathodic areas. Attack is often nonuniform and limited to specific areas of the surface. The corrosion resistance of some alloy sheet can be improved by cladding the sheet with a thin layer of unalloyed aluminum; however, the aluminum must be anodic to the base metal. Aluminum performs poorly in direct contact with more noble metals in the presence of an electrolyte; galvanic attack of

aluminum may take place near the contact area.

21.3.5 Gases and Aluminum

Hydrogen is appreciably soluble in both solid and molten aluminum. Other gases reported to be present occur when nonmetallics in the metal react with the environment. Molten aluminum reacts readily with carbon monoxide and carbon dioxide; it also reacts with water vapor in the atmosphere, adsorbed water, water present in hydrated oxide films on scrap, and water adsorbed on or combined in refractories. Solid aluminum reacts with moisture in the atmosphere of a furnace to form oxides and hydrogen. Hydrogen is considerably less soluble in solid than in molten aluminum. The gas diffuses out of the metal at a rate determined by the temperature. However, when the reaction of aluminum with water vapor leads to a high activity of hydrogen at the solid-gas interface, the concentration gradient can be reversed. As a result, the rate of outgassing is decreased and a higher level of hydrogen is retained in the metal. In solid aluminum, hydrogen in excess of the solution limit can precipitate as H_2 at grain boundaries, thus lowering the hydrogen ion concentration and in turn further facilitating the diffusion of hydrogen ions from the interface into the metal.

21.4 Production

The only method now used industrially to produce primary aluminum is the Hall-Héroult process. Production of aluminum before its development was discussed previously in this article. Alternate means of producing aluminum are treated in Section 21.4.5.

21.4.1 History of the Electrolytic Reduction of Alumina

The technological elements of the process—electrolysis of fused salts to produce metals (including aluminum), the use of cryolite as a flux to dissolve alumina, and the use of carbon

electrodes—had been exploited for some time prior to 1886. The workable electrolytic process was discovered independently, and almost simultaneously, in early 1886 by CHARLES MARTIN HALL in Oberlin, Ohio, and PAUL L. T. HÉROULT in Gentilly, France. Both these young scientists were familiar with the work of SAINT-CLAIRE DEVILLE.

In less than three years, the invention had been implemented industrially in North America and in Europe. In November 1888 aluminum was first produced commercially by the electrolytic reduction of alumina by HALL and others in a company that later was to become the Aluminum Company of America. At about the same time, HÉROULT was associated with a company (later to be known as Alusuisse) that operated aluminum electrowinning cells at Neuhausen, Switzerland.

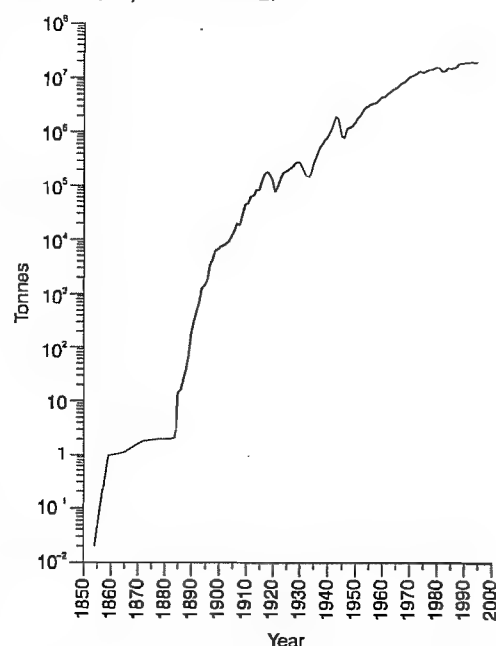


Figure 21.2: Annual world production of primary aluminum 1854–1996.

KARL JOSEF BAYER, an Austrian chemist, was issued a patent, DE 43977, in July 1887 for an improved method of producing alumina from bauxite. Bauxite, discovered by P. BERTHIER in 1821, is named for Les Baux, the village in the south of France near which it was

first found. With the development of a process to produce pure aluminum oxide from this abundant ore, the technology was then complete to spur rapid growth of the aluminum industry in Europe and North America in the last decade of the 19th century. The increase in the production of primary aluminum during the past hundred years is shown in Figure 21.2.

21.4.2 Raw Materials

Carbon. In the industrial electrowinning (separation by electrolysis) of aluminum, part of the energy for reducing alumina is supplied as electricity and part comes from consumption of the carbon *anode*. Carbon is also used as the cathode lining. Because 0.4–0.5 kg of anode is consumed for each kilogram of aluminum produced, this represents the major carbon requirement. Because the ash from the carbon will contaminate either the aluminum produced or the electrolyte, high-purity carbon is desirable. Certain impurities, such as vanadium, are particularly harmful in that they catalyze air burning of the carbon. Other impurities, such as phosphorus, accumulate in the electrolyte and undergo cyclic redox reactions (partial reduction followed by reoxidation), consuming electric current without producing product. The coke residue from petroleum refining is quite pure and, therefore, has been the major source of carbon for anodes. The structure of petroleum coke varies depending on the nature of the petroleum feedstocks used at the refinery, the refinery flowstream, and the coking conditions used. This coke produced at about 500 °C requires calcining at about 1200 °C to remove volatile constituents and increase its density before it is blended into the anode mix. After calcination, the coke is ground and mixed with crushed spent anodes and sufficient coal-tar pitch to allow molding into anode blocks by pressing or by vibrating. They are baked at 1000–1200 °C, causing the pitch to carbonize, forming strong carbon blocks. These blocks are made with one or more sockets into each of which is fastened a steel stub by pouring cast iron around it. These stubs both conduct

electric current into the anode and support the anodes in the cell. The cost of petroleum coke for prebaked carbon anodes in the United States was about \$0.20/kg (\$0.09/pound) in 1996.

Anthracite has been the major constituent in the cell *cathode* blocks, although graphite and metallurgical coke have been used to some extent. The anthracite is calcined at 1200 °C or higher, crushed and sized, mixed with coal-tar pitch, molded into blocks, and baked. These blocks, mortared together with a carbonaceous seam mix, form the pot lining, which is the container for both the aluminum and the electrolyte. High purity is not as important for the cathode blocks because leaching of impurities is very slow. Consumption of cathode carbon amounts to 0.02–0.04 kg of carbon per kilogram of aluminum produced. The life of a pot (typically 2–6 years) generally is terminated by failure of the carbon pot lining.

Aluminum Oxide. Depending on its purity and losses in handling, 1.90–1.95 kg of alumina are consumed in producing 1 kg of aluminum. The cost of alumina at United States smelting facilities was \$0.16–0.20/kg (\$0.07–0.09/pound) in 1996. The preparation of metallurgical alumina and its required physical and chemical properties are discussed in Section 21.10.1.

Electrolyte Materials. The electrolyte for electrowinning aluminum is basically a solution of aluminum oxide in cryolite. The presence of cryolite is essential for dissolution of alumina. Cryolite usually comprises more than 75% of the electrolyte which typically also contains calcium fluoride (4–8%), excess aluminum fluoride (5–15%), alumina (1–6%), and sometimes lithium fluoride (0–5%) and magnesium fluoride (0–5%). These additives lower operating temperature and increase current efficiency.

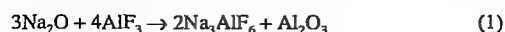
The mineral cryolite is the double fluoride of sodium and aluminum and has a stoichiometry very near the formula Na_3AlF_6 and a melting point of about 1010 °C. It has been found in substantial quantities only in Green-

land, and was mined extensively there in the early 20th century but now is essentially exhausted. Synthetic cryolite can be produced by reacting hydrofluoric acid with an alkaline sodium aluminate solution:



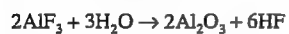
Cryolite also can be recovered from used pot linings. The lining is crushed and treated with dilute sodium hydroxide solution to dissolve fluorides. After being filtered, the solution is neutralized with carbon dioxide to precipitate the cryolite.

Cryolite is produced directly in reduction cells by reaction of the soda impurity in the feed alumina with added aluminum fluoride:



Electrolyte generated by the above reaction must be tapped from the cells periodically. In modern smelters with dry scrubbing equipment for fume treatment and cell lives greater than 3 years, cryolite is a by-product rather than a raw material in producing aluminum. Synthetic cryolite could be purchased in the United States for \$500–600/t in 1983.

Aluminum fluoride, AlF_3 , may comprise as much as 15% of the electrolyte in excess of the amount represented by the cryolite composition. Aluminum fluoride is consumed during normal operation by three major mechanisms. First, losses of aluminum fluoride by vaporization are appreciable; the most volatile species present in the electrolyte is sodium tetrafluoroaluminate, NaAlF_4 , having a partial pressure of 200–600 Pa over the operating melt, depending on composition and temperature. Second, aluminum fluoride is depleted by hydrolysis:



Aluminum fluoride is also consumed by the evolution of carbon tetrachloride during anode effects.

And finally, aluminum fluoride is consumed by reaction with the soda present in feed alumina (Equation 1).

Fume capture and scrubbing efficiencies have improved in recent years at aluminum smelters. Fluoride previously lost by vaporiza-

tion of NaAlF_4 and hydrolysis of bath is now almost completely recycled to the cells. Nevertheless, aluminum fluoride consumption amounts to 0.01–0.04 kg AlF_3 per kilogram of aluminum product. In 1996 technical anhydrous aluminum fluoride could be purchased in the United States for about \$350/t.

21.4.3 Hall-Héroult Cell

All commercial production of aluminum today is done in Hall-Héroult cells. Two major types of cells are currently in use: those employing prebaked carbon anodes and those employing self-baking Söderberg anodes. The Hall-Héroult cell with *prebaked anodes* is shown in Figure 21.3. Essentially pure alumina is fed into the previously discussed cryolite base electrolyte. Electric current deposits aluminum into a pool of molten aluminum held under the electrolyte in the carbon lined cavity of the cell. Oxygen from the alumina deposits electrolytically onto the carbon anode dipping into the electrolyte and reacts with (burns) the anode. Cells typically range from 9 to 14 m long, 3 to 5 m wide, and 1 to 1.2 m high. Thermal insulation surrounds the carbon lining of the cell to control heat losses. Although carbon is the material known to withstand best the combined corrosive action of molten fluorides and molten aluminum, even carbon would have a very limited life in contact with the electrolyte at the sides of the cell were it not protected by a layer of frozen electrolyte. The thermal insulation is adjusted carefully to maintain a protective coating on the walls but not on the bottom, which must remain substantially bare for good electrical contact. Steel collector bars in the carbon cathode conduct electric current from the cell. These bars are inserted into holes that have been sized carefully so that thermal expansion forms a tight electrical contact, or cemented in place with a carbonaceous cement containing metal particles, or bonded in place with cast iron.

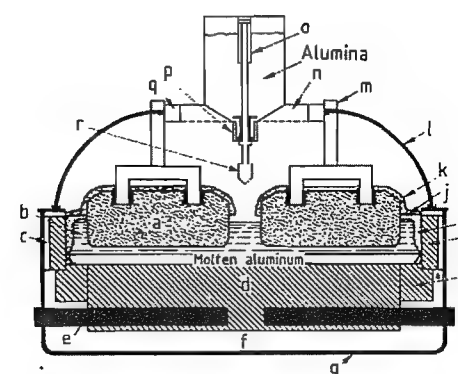


Figure 21.3: Hall-Héroult cell with prebaked anodes: a) Carbon anode; b) Electrolyte; c) Insulation; d) Carbon lining; e) Current collector bar; f) Thermal insulation; g) Steel shell; h) Carbon block; i) Ledge; j) Crust; k) Alumina cover; l) Removable covers; m) Anode rods; n) Fume collection; o) Air cylinder; p) Feeder; q) Current supply; r) Crust breaker.

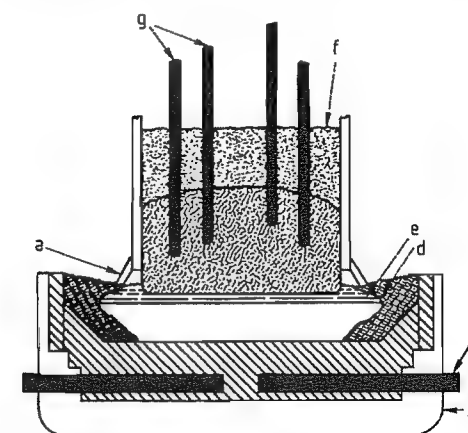


Figure 21.4: Aluminum electrolyzing cell with Söderberg anode: a) Manifold gas; b) Steel shell; c) Current collector bars; d) Frozen ledge; e) Molten electrolyte; f) Coke and tar paste; g) Current supplying pins.

The electrical resistivity of prebaked anodes ranges from 0.005 to 0.006 Ωcm . Current density at the anode race is 0.6–1.3 A/cm^2 .

The *Söderberg anode* (Figure 21.4) uses a premixed “paste” of petroleum coke and coal-tar pitch. This mixture is added at the top of a rectangular steel casing that is typically 6–8 m long, 2 m wide, and 1 m high. Heat from the electrolyte and heat from the electric current

passing through the anode bakes the carbonaceous mix as it progresses through the casing.

The baked portion extends past the casing and into the molten electrolyte. Baked mix replaces anode being consumed at the bottom surface. Electric current enters the anode through either vertical or sloping steel spikes. These spikes are pulled and reset to a higher level as they approach the lower surface. Söderberg anodes have an electrical resistivity about 30% higher than that of prebaked anodes. Because of the resulting lower power efficiency and the greater difficulty in collecting and disposing of baking fumes, Söderberg anodes are being replaced by prebaked anodes, even though the former save the capital, labor, and energy required to manufacture the latter.

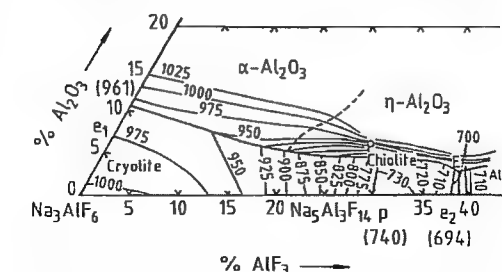


Figure 21.5: The Na_3AlF_6 - AlF_3 - Al_2O_3 system [17].

21.4.3.1 Electrolyte

Pure cryolite melts at about 1010 °C. Alumina and other additives lower the melting point, allowing operation at 940–980 °C. The cryolite–aluminum fluoride–alumina system (Figure 21.5) [17] has binary eutectic points at 961 °C and 694 °C and a ternary one at 684 °C. Calcium fluoride and lithium fluoride further reduce the liquidus temperature (Figures 21.6 [18] and 21.7 [19]). Calcium fluoride is seldom added intentionally. Because of a small amount of calcium oxide impurity in the alumina, it attains a steady-state concentration of 3–8% in the melt. At this level calcium is codeposited into the aluminum and emitted in the off-gas at a rate equal to its introduction. Magnesium fluoride accumulates to 0.1–0.3%, in the electrolyte by the same mechanism as calcium fluoride. Some opera-

tors add up to 5% MgF_2 because it expels carbon dust from the electrolyte by decreasing the electrolyte's ability to wet carbon.

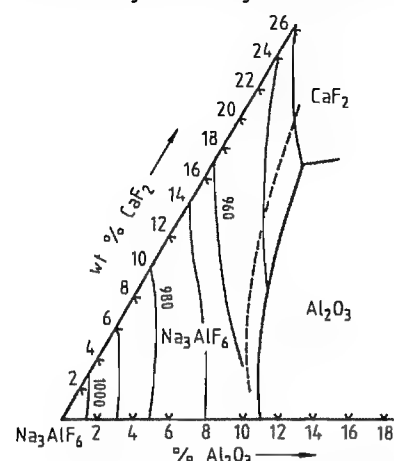


Figure 21.6: The Na_3AlF_6 - Al_2O_3 - CaF_2 system [18].

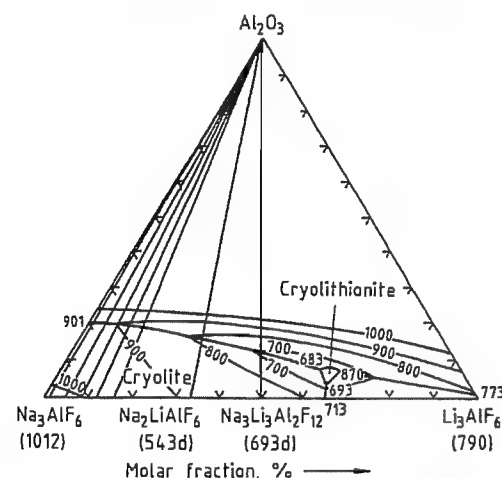


Figure 21.7: The Na_3AlF_6 - Li_3AlF_6 - Al_2O_3 system [19].

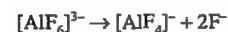
Calcium fluoride, in addition to lowering the liquidus temperature, decreases the vapor pressure and solubility of reduced species in the electrolyte for better current efficiency. Detrimentally, it lowers alumina solubility and electrical conductivity and increases density, viscosity, and surface tension of the electrolyte. Lithium fluoride in addition to lowering the melting point, decreases the vapor pressure, density, reduced species solubility, and viscosity; it also increases electrical conduc-

tivity. The only negative effect appears to be lowered alumina solubility. Its high cost, however, requires that its benefits be weighed against the price. Aluminum fluoride decreases solubility of reduced species and lowers surface tension, viscosity, and density. It has the undesirable effects of decreasing alumina solubility and electrical conductivity and increasing vapor pressure. Aluminum fluoride acts as a Lewis acid with sodium fluoride acting as a Lewis base. Neutrality has been defined arbitrarily as a molar ratio of sodium fluoride to aluminum fluoride of 3:1. Control of electrolyte acidity or the $\text{NaF}:\text{AlF}_3$ molar ratio, referred to as the *cryolite ratio* (R_c) is of importance to cell operation. Lithium fluoride is a slightly weaker Lewis base than sodium fluoride. Magnesium fluoride is a weak Lewis acid.

Ionic Structure of the Melt. There is general agreement that molten cryolite is completely ionized to sodium ions and hexafluoroaluminate ions:

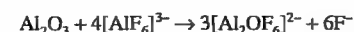
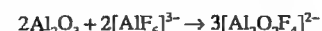


Also it is well established that the hexafluoroaluminate ion dissociates further:



At 100 °C, $[\text{AlF}_6]^{3-}$ is about 25% dissociated [20]. Dissociation increases with decreasing cryolite ratio [20].

The nature of the species formed when alumina is added is not so well established. Combination of the results of cryoscopic measurements, Raman spectrographic data, and equilibrium studies and vapor pressure measurements (reviewed in [20]) leads to the conclusion that $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$ and $[\text{Al}_2\text{OF}_6]^{2-}$ are the two major oxygen-containing ions in the melt. Possible reactions for their formation are:



21.4.3.2 Electrode Reactions

Cathode Reaction. Even though Na^+ is the principal current carrier, it does not discharge

at the cathode. The reversible electromotive force for the formation of liquid aluminum is about 0.24 V lower than that for the formation of sodium gas at 101.3 kPa (1 atm) for the range of compositions and temperatures used industrially. Aluminum-containing ions, mainly $[\text{AlF}_4]^-$, must diffuse to the cathode interface where they are reduced, leaving behind fluoride ions. Electrical neutrality is maintained by the electrical transport to the cathode of sodium ions (and lithium ions when LiF is present). This results in a diffusional flux of NaF away from the cathode and an increase in the $\text{NaF}:\text{AlF}_3$ ratio at the cathode interface.

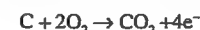
The cathode overvoltage can be represented by [21]:

$$\eta_{cc} = \frac{RT(1.375 - 0.125R_c)}{1.5F} \ln \frac{i}{i^0} \quad (2)$$

where R is the gas constant, T is the temperature (K), R_c is the mole ratio $\text{NaF}:\text{AlF}_3$, F is the Faraday constant, and i is the electrode's current density (in A/cm^2).

Although this relationship mathematically looks like activation overvoltage, actually the cathode overvoltage is caused by an increase in the $\text{NaF}:\text{AlF}_3$ ratio at the aluminum surface [22]. Using Fick's first law, the resulting concentration gradients were calculated and good agreement was found between the measured overvoltages and the electromotive forces between the two aluminum half-cells, one containing electrolyte of the bulk composition and the other, electrolyte corresponding to the calculated interfacial composition.

Anode Reactions. The primary anode reaction can be written:



However, O_2 ion is not present in the bulk electrolyte; instead, oxygen is present as structurally large complexes, i.e., $[\text{Al}_2\text{OF}_6]^{2-}$ and $[\text{Al}_2\text{O}_2\text{F}_4]^{2-}$. Thermodynamically, oxygen depositing onto carbon at 950–1000 °C should equilibrate to about 99% CO and 1% CO_2 . However, based on either net carbon consumption or the volume of gas produced, the primary anode product is essentially all CO_2 . The high anodic overvoltage implies that reac-

tion kinetics cause this surprising displacement from thermodynamic equilibrium. Rotating disk [23] and impedance [24] measurements indicate that there is a small diffusional overvoltage, probably caused by reaction within the pores of the electrode. Using the general treatment for heterogeneous reaction control [25], overvoltage data can be expressed by the relationship:

$$\eta_{sa} = \frac{\nu RT}{pnF} \ln \frac{i}{i^0} \quad (3)$$

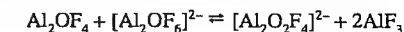
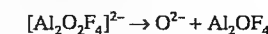
where ν is the number of executions of rate-controlling steps to produce one overall step, p is the reaction order, n is the number of electrons transferred in one overall step, and i^0 is the reaction-limiting current density.

The reaction order, $p = 0.57$, was found from measurements of overvoltage versus current density [26]. In industrial practice, the reaction order ranges from 0.4 to 0.6, varying with carbon reactivity and porosity. The reaction-limiting current density i^0 goes from 0.0039 to 0.0085 A/cm^2 as alumina concentration varies from 2 to 8%. The reaction order also has been determined [26] from the rate of change of the limiting current with reactive species concentration and a similar value obtained:

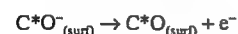
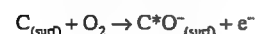
$$p = \frac{d \ln i^0}{d \ln c_{\text{Al}_2\text{O}_3}} = 0.56$$

Measurements [27] of the ordinary combustion of graphite have shown that when oxygen reacts both in pores and on the surface, a chemical reaction of approximately half-order results. Linear sweep voltammograms showed voltage peaks with increasing current density corresponding to discharge of CO_2 , COF_2 , and CF_4 [28].

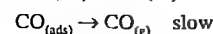
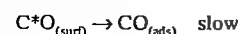
The following anode reaction mechanism is consistent with these observations. Oxyfluoride ions dissociate within the double layer to oxygen ions:



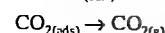
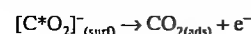
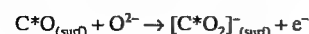
Oxygen ions discharge upon the carbon surface (surf) forming an activated complex, CO:



The activated complex converts very slowly to CO_(g) through an adsorbed (ads) intermediate:



Carbon burning in pure oxygen at 940–970 °C has a combustion rate equivalent to between 0.1 and 0.2 mA/cm². One would expect this reaction to proceed at a similarly slow rate. As available surface sites become covered with C*O, oxygen is deposited at higher energy (overvoltage) onto a carbon site already bonded to oxygen, producing unstable [C*O₂]⁻, which breaks carbon to carbon bonds almost immediately as it is formed:



The adsorbed CO₂ quickly desorbs as CO_{2(g)}. This mechanism explains both the high anodic overvoltage and the primary production of CO₂ instead of the thermodynamically favored CO.

When there is insufficient alumina dissolved in the electrolyte, the cell experiences a phenomenon called *anode effect*. Bubbles grow larger and larger on the anode until the electrolyte no longer wets the anode. With a constant potential the current falls to a low value; but with the constant current source used industrially, the cell potential rises to ≥ 30 V. Current then penetrates the gas film by a multitude of small electric arcs or sparks. The gas produced at the anode changes from CO₂ to CO, with significant quantities (3–25%) of CF₄ and minor amounts of C₂F₆ generated. Fluorocarbon compounds most likely deposit on the surface of the anode and trigger the anode effect. As alumina is depleted, anode overvoltage increases. At about 1.2 V anode overpotential, sufficient thermodynamic ac-

tivity of fluorine is produced to cause fluorine to bond to the carbon. Even though these low-surface-energy carbon–fluorine compounds decompose on the surface to CF₄ and C₂F₆ at cell temperature, their rate of formation can exceed the rate of thermal decomposition, producing high coverage. Once the cell is on anode effect, restoring the alumina concentration is not sufficient to return it to normal operation. The gas film must be broken by splashing aluminum, by interrupting the current momentarily, or by lowering the anodes to expose new areas not contaminated with fluorine.

21.4.3.3 Current Efficiency

According to Faraday's law, 1 kA·h of electric current should produce 0.3356 kg of aluminum, but only 85–96% of this amount is obtained. The principal loss mechanism is recombination of anodic and cathodic products. Reduced species go into solution in the electrolyte at the aluminum–electrolyte interface (Figure 21.8). The equilibrium (Equation 4) produces a thermodynamic activity of sodium in the melt, whereas Equation (5) produces an activity of aluminum monofluoride.

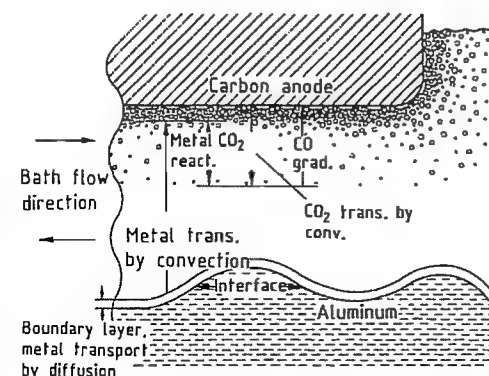
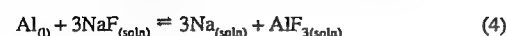


Figure 21.8: Current efficiency loss by metal reoxidation.

Metal going into solution must first diffuse through the metal–electrolyte boundary layer (Figure 21.8). The metal is then transported by convection to the vicinity of the anode. Here it

reacts with carbon dioxide. Chemical reactions appear to be fast compared to mass transport. The rate-controlling step is usually assumed to be diffusion of dissolved metal through the boundary layer at the metal–electrolyte interface. However, mixed control, with diffusion at both the aluminum–electrolyte interface and the bubble–electrolyte interface being important, has been reported [29].

There are several mechanisms accounting for additional minor losses in current efficiency. New cell linings absorb sodium, with Equation (4) maintaining an equilibrium activity of sodium. Fortunately, the lining saturates early in the cell's life but until this occurs, current efficiency is low. The sodium metal dissolved in the electrolyte imparts electronic conductivity to the electrolyte [30]. This may cause between 1 and 3% loss in current efficiency, the higher value being associated with higher ratios of NaF:AlF₃. Such elements as phosphorus and vanadium, which can be reduced partially at the cathode and then reoxidized at the anode, may lower efficiency.

21.4.3.4 Cell Voltage

The voltage of a Hall–Héroult cell is made up of a number of components:

$$E_{cell} = E^0 + \eta_{CA} + \eta_{CC} + \eta_{SA} + \eta_{SC} - I(R_A + R_B + R_C + R_X)$$

where E^0 is the thermodynamic equilibrium voltage described in Section 21.4.4; η_{CA} is the concentration overpotential at the anode; η_{SA} is the surface overpotential at the anode described by Equation (3); η_{CC} is the concentration overpotential at the cathode described by Equation (2); η_{SC} is the surface overpotential at the cathode, generally negligible; I is the total cell current; R_A is the electrical resistance of the anodes or anode; R_B is the effective resistance of the bath, allowing for fanning out of current as it flows from anode to cathode and the increased bath resistivity caused by gas bubbles; R_C is the cathode resistance; and R_X is the resistance external to the cell but included in calculating power consumption.

The anode concentration overpotential can be calculated by:

$$\eta_{CA} = \frac{RT}{2F} \ln \frac{i_c}{i_c - i}$$

The quantity i_c is the concentration-limited current density and it varies between 1.0 ± 0.5 A/cm² at 1% Al₂O₃ and 15 A/cm² at 8% Al₂O₃. The specific power consumption in kilowatt-hours per kilogram of aluminum can be calculated:

$$\text{kWh/kg} = 298.06 \frac{E_{cell}}{\% \text{ CE}}$$

where % CE is the percentage current efficiency or Faraday efficiency and E_{cell} is the cell voltage.

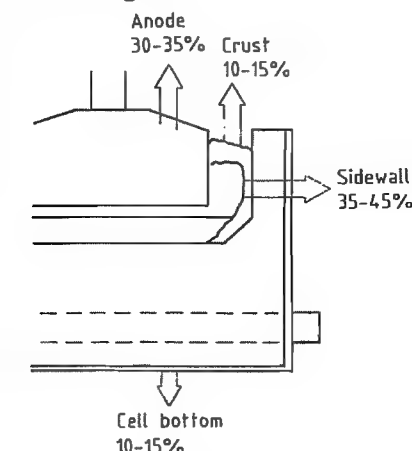


Figure 21.9: Cell heat loss distribution [33].

21.4.3.5 Heat Balance

Heat balance considerations are important in designing and operating a cell at the optimum temperature. Calculation is complicated by simultaneous heat flow and heat generation in conductors that carry electric current into and out of the cell. More than 50% of the heat loss may occur through the anodes and tap crust. The sidewalls must be protected from erosion by a ledge of frozen electrolyte maintained by extracting the exact amount of heat required for the desired ledge thickness. These calculations have been described [31, 32]. The complex geometry and the interaction be-

tween heat flow and electrical flow generally require a computer using either a finite element or finite difference technique for heat balances. Figure 21.9 [33] shows a typical heat loss distribution for a center-fed cell and Figure 21.10 [33], the typical temperature distribution.

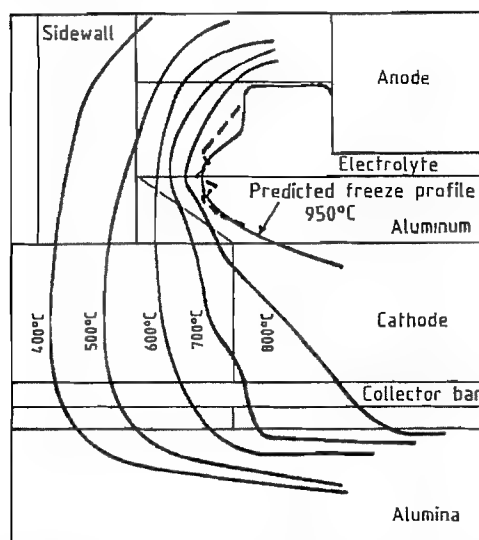


Figure 21.10: Cell lining isotherms [33]. Dashed line: measured profile.

21.4.3.6 Fluid Dynamics

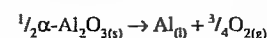
The large electric currents used in modern cells generate relatively strong magnetic fields within the cell. These magnetic fields interact with electric currents and exert Lorentz forces, producing movement of liquid conductors. Three types of magnetic disturbances have been observed: a vertical or static displacement of the metal pad, a circulating flow within the metal pad with velocities as high as 20 cm/s, and finally a wave motion in the metal pad. The last is probably the most harmful because waves may lead to electrical short circuiting. Calculation of the magnetic fields and electric current flow patterns is complicated. Computer programs have been designed to make these calculations and describe the fluid-dynamic consequences. These calculations have been refined to the point where

today, cells of over 3.0×10^5 A have been designed and operated with high efficiency. Natural convection caused by temperature gradients or composition differences in the electrolyte are insignificant compared with the movement induced by magnetic forces and gas bubbles. Gas bubbles produce significant stirring in the electrolyte and are the dominant force in bath movement, whereas electromagnetic forces predominate in metal pad movement.

21.4.4 Thermodynamic Considerations

Thermodynamic data used in the following section are from the *JANAF Thermochemical Tables* [34].

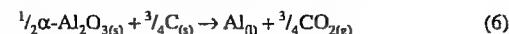
For pure α -alumina, reduction to aluminum can be represented:



At 960 °C (1233 K), $\Delta G_{1233}^0 = +642.1$ kJ and

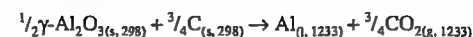
$$\Delta H_{1233}^0 = +845.6$$
 kJ

In the industrial production of aluminum, a portion of the energy is supplied by the combustion of carbon anodes to carbon dioxide. The overall cell reaction can be represented:



At 960 °C, $\Delta H_{1233}^0 = +549$ kJ

Additional energy is required to heat alumina and carbon from room temperature to operating temperature. The alumina fed to the cell usually is not pure α -alumina. For γ -alumina, the overall process can be represented:



The enthalpy requirement for transformation of the reactants at 25 °C (298 K) to products at 960 °C (1233 K) is:

$$\Delta H_{r(35)} = \Delta H_{1233}^0 + \frac{1}{2}(H_{1233}^0 - H_{298}^0)\gamma\text{-Al}_2\text{O}_3 + \frac{3}{4}(H_{1233}^0 - H_{298}^0)\text{C}_{(s)} = 606.4$$
 kJ

This value corresponds to a theoretical energy requirement of 6.25 kWh per kilogram of aluminum produced.

The reversible cell potential (decomposition voltage) for Reaction (6) can be calculated from the relation:

$$\Delta G_{1233}^0 = -nFE_{\text{sat}, 1233}^0 \quad (7)$$

where ΔG_{1233}^0 is the Gibbs free energy change for reaction (6), 3.448×10^5 J; n is the number of electrons per unit cell reaction, i.e., 3; F is the Faraday constant, 96.487 kJ V⁻¹ mol⁻¹; and $E_{\text{sat}, 1233}^0$ is the standard electrode potential, in volts, at 960 °C for the reaction with all reactants and products at unit activity. Substituting the appropriate values into Equation (7) and solving for the cell potential:

$$E_{\text{sat}, 1233}^0 = 1.191$$
 V

The above decomposition potential applies to electrolyte saturated with alumina at 950 °C. The decomposition potential from melts with alumina activity less than unity can be calculated [21] from the equation:

$$E^0 = E_{\text{sat}}^0 + \frac{RT}{6F} \ln a_{\text{Al}_2\text{O}_3}$$

The activity of alumina in cryolite-base melts can be approximated [21] from the equation:

$$a_{\text{Al}_2\text{O}_3} = (c_{\text{Al}_2\text{O}_3}/c_{\text{Al}_2\text{O}_3}^*)^n$$

where $c_{\text{Al}_2\text{O}_3}$ is the concentration of alumina in the electrolyte, in %, $c_{\text{Al}_2\text{O}_3}^*$ is the saturation concentration of alumina, in %, and $n = 1.5$ for $c_{\text{Al}_2\text{O}_3} > 0.45 c_{\text{Al}_2\text{O}_3}^*$ and $n = 3$ for dilute solutions.

21.4.5 Alternate Processes

Although the Hall-Héroult process has gained industrial dominance, it has several inherent disadvantages. The most serious are the large capital investment required and the high consumption of costly electrical power. There are also the costs of the Bayer alumina refining plant and of the carbon anode plant. Many of the aluminum-producing countries must import alumina or bauxite. The supply of petroleum coke is limited. These deficiencies have spurred research to find alternate processes.

The earliest commercial process for producing aluminum was sodiothermic reduction of aluminum halides. Reduction of aluminum chloride by manganese has been studied and

reviewed [35]. However, neither can compete with the Bayer/Hall-Héroult process. Many attempts have been made at direct carbothermic reduction of alumina but these have resulted in very low yields, owing to the formation of solid aluminum carbide, aluminum suboxide vapor, and aluminum vapor that reacts with carbon monoxide as the temperature drops on the way from the furnace. Yields as high as 67% can be obtained by staging the reactions to produce aluminum carbide at 1930–2030 °C, which then reacts with alumina to produce aluminum and carbon monoxide at 2030–2130 °C [35].

Better yields result from adding to the furnace a metal (or a metal oxide that is subsequently reduced to a metal), such as iron, silicon, or copper, to alloy with the aluminum and lower its vapor pressure. Of course it is then necessary to extract the aluminum from the alloy. In principle this can be accomplished by electrolytic refining, by fractional crystallization, or by monohalide distillation. In the latter process the aluminum extraction takes place at 1000–1400 °C:



The AlCl gas is transported to a cooler zone, 600–800 °C, where pure aluminum is formed:



These combined processes to date have proved noncompetitive. Selective solution of aluminum from the alloy by using a volatile metal, such as mercury, lead, bismuth, cadmium, magnesium, or zinc, has been investigated. Following extraction, the volatile metal is distilled, leaving pure aluminum. If FeAl₃, TiAl₃, or Al₄C₃ is formed, neither electrolysis nor volatile metal extraction will remove the aluminum from the compound.

The aluminum vapor pressure can be lowered also by alloying the aluminum with aluminum carbide. Over 40% aluminum carbide is soluble in aluminum at 2200 °C [35]. This observation led to a process in which an alloy of aluminum and aluminum carbide was produced at 2400 °C. When this alloy was tapped from the furnace and allowed to cool slowly,

the aluminum carbide crystallized into an open lattice, the interstices of which were filled with pure aluminum. Pure aluminum was then removed either by leaching with molten chloride fluxes or by vacuum distillation. The aluminum carbide residue was recycled to the arc furnace. Alternately, the aluminum carbide could be distilled destructively above 2200 °C to produce aluminum and a residue of pure graphite.

In a joint project with the U.S. Department of Energy concluded in 1983, Alcoa investigated producing aluminum-silicon alloy in a blast furnace. The required high temperature was obtained by using a pure oxygen blast. Using a low-pressure blast furnace to produce an aluminum-silicon alloy was found to be infeasible because of severe bridging and interruption of the burden movement caused by total reflux of Al, Al₂O₃, and SiO vapors. Addition of iron improved operation but required an improved technique for extracting the aluminum from the dilute aluminum alloy. An alloy having higher aluminum content could be obtained if a significant portion of the process energy was supplied by electrical power. The aluminum blast furnace concept aims for a low-silicon, high-iron alloy. This improves the blast furnace efficiency but complicates extraction of pure aluminum from the alloy.

In 1976 Alcoa described a smelting process wherein aluminum chloride, dissolved in a molten sodium chloride-lithium chloride electrolyte, was electrolyzed in a bipolar electrode cell to produce aluminum and chlorine. The chlorine was recycled to a fluid-bed chemical reactor, where it reacted with alumina, pyrolytically coated with carbon from fuel oil, to produce aluminum chloride, carbon dioxide, and carbon monoxide. This reaction was highly exothermic. The aluminum chloride was desublimed to separate it from the gas and recycled to the cell to produce more aluminum and chlorine. This process required 30% less electrical power than their best Hall-Héroult cells. Because the entire process is a closed system, it was also environmentally more attractive than the Hall-Héroult process. Problems with the chemical plant and high

maintenance caused the demonstration plant to be shut down in 1982.

21.5 High-Purity Aluminum

The Hall-Héroult process has produced aluminum with a purity as great as 99.95%. Other techniques, such as electrolytic refining or fractional crystallization, are required to produce purer metal. Alcoa developed a three-layer electrolytic aluminum-refining cell in the 1920s. Copper was added to the bottom layer of impure aluminum to increase its density above that of the fused salt electrolyte. The electrolyte contained 25–30% sodium fluoride, 30–38% aluminum fluoride, and 30–38% barium fluoride to increase the electrolyte's density so that pure aluminum would float to the top. Electric current entered the anode alloy through carbon or graphite blocks at the bottom of the cell and left through graphite electrodes dipping into the high-purity aluminum on top. Aluminum was transported preferentially. Metals more difficult to oxidize than aluminum remained in the anode or alloy layer, and metals more difficult to reduce than aluminum remained in the electrolyte. A ledge of frozen electrolyte on the carbon sidewalls prevented electrical short circuiting between the floating pure aluminum layer and the carbon wall. The cell operated at 950–1000 °C and produced 99.98% pure metal.

In 1932 the Pechiney Company in France operated a cell using a fluoride-chloride electrolyte and nonconducting magnesite brick sidewalls. The electrolyte consisted of 17% sodium fluoride, 23% aluminum fluoride, and 60% barium chloride. The cell operated at 750 °C and produced 99.995% pure aluminum. An all-fluoride electrolyte (18% sodium fluoride, 48% aluminum fluoride, 16% calcium fluoride, 18% barium fluoride) also can be used in magnesite-lined cells. Modern electrolytic refining cells (Figure 21.11) add a segregation sump [36]. The sump, normally operated at least 30 °C cooler than the aluminum alloy anode, serves as a charging port for aluminum and permits impurity removal. As

impurities concentrate in the bottom layer, saturation is reached and crystals form in the cooler sump area, where they can be removed. This procedure greatly extends the operating life of the cell.

Fractional crystallization also is used commercially to refine aluminum. As aluminum freezes most impurities preferentially concentrate in either the liquid or the solid. A molten zone is moved along an aluminum bar in zone refining. Impurities that lower the melting point of aluminum concentrate at one end of the bar, whereas impurities that raise the melting point concentrate at the other end. After several passes the ends are removed, leaving a middle portion of high-purity aluminum.

Super-purity aluminum is produced by another fractional crystallization process [37]. In the first step, peritectic elements are removed from molten aluminum by reacting them with boron to form borides, which are precipitated and settled before the metal is transferred to a second furnace. Here the surface of molten aluminum is cooled with forced air, causing metal to crystallize. When the furnace is nearly filled with crystals, the remaining impure aluminum is drained. Then the crystals are remelted to yield very pure metal. Aluminum of purity higher than 99.995% has been produced from 99.9% pure smelting-grade aluminum by this process.

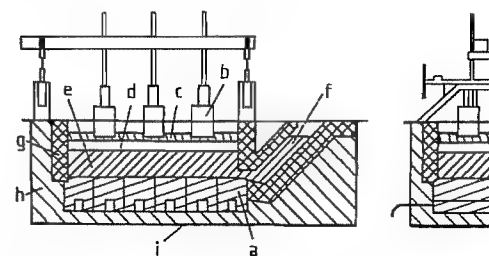


Figure 21.11: Longitudinal and cross sections of 15 000-ampere aluminum refining cell: a) Anode (carbon blocks); b) Cathode (graphite electrodes); c) Refined aluminum; d) Electrolyte; e) Alloy serving as anode; f) Segregation sump; g) Magnesite brick; h) Refractory block; i) Iron shell.

21.6 Aluminum Casting: Remelt Ingot

Metal tapped from the Hall-Héroult cell may be treated in one of several ways. First, it may be transported in the molten state to a holding furnace, where, along with solid scrap, it is alloyed, fluxed, filtered, and cast into a form suitable for fabrication by rolling, forging, etc., or for remelting by a foundry. It may be transported further (over distances up to 200 km) on trucks, equipped with well-insulated containers to prevent freezing, to a foundry where it is alloyed and used to make shaped castings. Both these methods of utilizing the molten metal are favored because energy required for remelting is conserved.

Alternatively, where ingot casting facilities or foundries are not nearby, metal is cast using cast iron molds into "primary" ingots for remelting. Generally, these unalloyed remelt ingots come as stackable 22-, 340-, or 680-kg ingots. Casting machines, such as the one illustrated in Figure 21.12, are often fully automated, with production rates of up to 20 000 kg/h. An important consideration is metal transfer from the ladle to the mold, which must be as quiescent as possible in order to minimize oxide contamination. Unalloyed ingot is sold in various purity grades, such as P0506 or P1520, depending on the maximum Si and Fe levels; e.g., P0506 is aluminum with 0.05% Si and 0.06% Fe maximum.

The larger sizes of unalloyed remelt ingot may be cast on semicontinuous DC (direct chill) casting equipment with a "T" cross section for ease of handling and stacking. This ingot usually is cut into lengths weighing approximately 340 kg.

Primary metal producers also make remelt ingot, which is prealloyed for the foundry industry. This is known as foundry ingot and generally is alloyed so that its composition lies within the limits of the alloy desired in the final shaped casting. Foundry ingot may be cast into open molds or continuously cast, cut to length, and stacked (Figure 21.13). The most common masses for this ingot, which is re-

melted in furnaces smaller than those used by wrought alloy producers, are approximately 14 kg and 22 kg. The general practice, where applicable, is to premodify and grain refine this foundry ingot. Also the molten metal is filtered and fluxed in a manner similar to that employed for wrought alloy ingot in order to insure optimum metal quality for the foundry user.

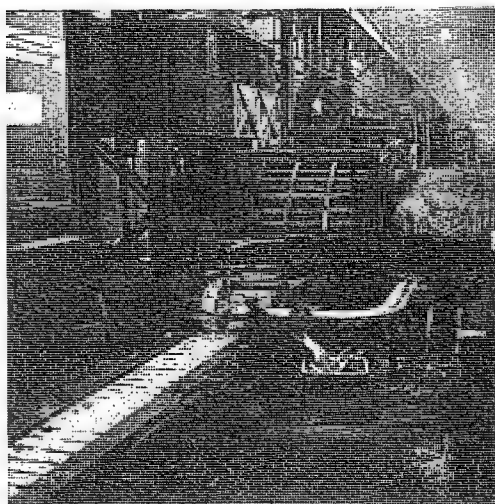


Figure 21.12: Casting machine for the production of open-mold remelt ingot (courtesy Gautschi Electrofours SA).

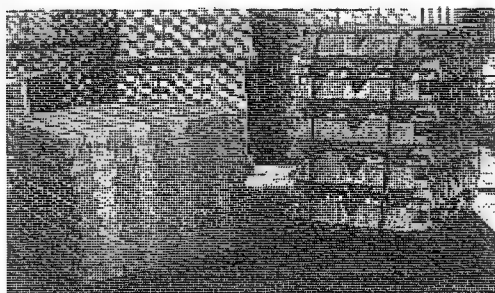


Figure 21.13: Different types of aluminum castings: a) Continuously cast "T" section bar-look; b) Open-mold foundry ingot.

21.7 Environmental Protection

In the primary production of aluminum there are three principal areas of environmen-

tal concern: air emissions, wastewater discharges, and solid waste. In the early years of the aluminum industry, most of the effort was directed toward controlling fluoride emission from the cells. The technology for fluoride control is now well established throughout the industry. Other significant air emissions from the anode production process have been controlled in recent years, or will be controlled through the Primary Maximum Achievable Control Technology (MACT) rule.

Wastewater effluent usually is not a major problem, except in those plants where wet processes are still used to scrub the air emissions from the cells and anode baking furnaces.

Cathode linings in aluminum cells are removed when lining failure occurs and large amounts of this material, called spent pot lining, must be discarded. Historically, spent potliner has been reclaimed for fluoride value, stockpiled, or landfilled. One company is now offering incineration treatment for potliner and many others are investigating incineration or fluoride recovery methods.

21.7.1 Air Emission

Cell Room Emission. Atmospheric emissions produced by an aluminum cell consist of particulate and gaseous fluoride (predominately HF), alumina, carbon dust, sulfur dioxide, carbon dioxide, and carbon monoxide. Typical values for total fluorides generated by the cell related to aluminum production range from 20 to 30 kg/t. Approximately the same amounts of alumina and carbon dusts also are produced. Sulfur dioxide varies according to the sulfur content of the coke used to prepare the anodes, whereas carbon monoxide emissions generally are less than 30×10^{-6} parts by volume.

Control of Cell Emissions. To control cell emissions, each cell is equipped with a closely fitted hood to collect the evolved gases, which are then ducted to pollution-control equipment. After air dilution the cell gas temperature ranges from 85 to 125 °C, depending on the ambient temperature. Both wet and dry

systems are employed to treat cell gas. Some of the older smelters use a combination of electrostatic precipitators for solids removal following by spray towers for removing hydrogen fluoride gas and some sulfur dioxide. Wet precipitators also are quite effective for collecting both gaseous and particulate fluorides; some sulfur dioxide also may be collected by wet precipitators.

Because of inherent disadvantages in wet systems, not the least of which is potential water pollution, new smelters employ *dry scrubbers* for controlling cell emission. A dry scrubber uses either a fluidized bed or direct injection of metal-grade alumina into the gas stream to remove the hydrogen fluoride gas by sorption. The larger the specific surface area of the alumina, the greater is its sorptive capacity for hydrogen fluoride.

The alumina usually is recovered from the gas stream by a fabric filter, which also removes the other entrained particulate species. Dry scrubber efficiencies are generally greater than 98 % for both the gaseous fluoride and the particulate matter. Dry scrubbers are considered to be state of the art control technology. The aluminum fluoride that is recycled to the cells represents a significant material recovery value.

Emissions from Anode Preparation. In the production of anodes, coke dust and pitch fumes are generated at the mixers and at the anode forming equipment. These emissions have historically been collected and exhausted from the area for worker protection. Current regulatory requirements in the US will require that these emissions be scrubbed using fluid coke or injected coke fines and baghouses. The collected pitch volatiles and coke will be recycled into the anode mix.

Pitch fumes, coke dusts, and fluorides are the chief pollutants in the waste gases from the anode baking furnaces. In most countries, limits are established for aluminum fluorides (0.05 kg per ton of aluminum) and particulate (dust) emissions, or opacity limits are set in lieu of particulate limitations.

Control Systems for Anode Baking Furnaces. The control systems for the baking furnace emissions are similar to those described for the cell, with both wet and dry systems being utilized. Fluidized alumina beds and alumina injection systems are used to control gaseous fluorides and hydrocarbons from most new furnaces. A major difference, however, is the need to cool the baking furnace gas in order to condense the hydrocarbons so that they can be extracted by the dusts on the bag filter.

21.7.2 Wastewater Discharge

Fume Collection Systems. Wastewater generation has been reduced drastically in recent years with the development of dry systems for controlling emissions. Some older facilities still rely on wet collection devices, which result in a wastewater stream contaminated with acid, fluoride, and organic material. Conventional treatment involves addition of lime and prolonged retention times (12 h to several days) for neutralization and removal of the calcium fluoride precipitate and a significant portion of the dissolved organic compounds, e.g., benz[a]anthracene, benzo[fluoranthene], benzo[a]pyrene, chrysene, and phenanthrene. At least 98 % of these can be removed by biologic treatment in a facultative lagoon that employs aerobic as well as anaerobic bacteria. Partial decomposition of the organic material occurs in the anaerobic bottom layer, whereas the aerobic bacteria present in the upper levels complete the degradation process. Other organic removal mechanisms in the facultative lagoon include skimming, adsorption, and sedimentation.

Sodium hydroxide and alum are used in place of lime for fluoride removal at some plants. This treatment creates a fluoride sludge that, after drying, can be used as a cryolite replacement in the aluminum cell.

Pot Wash Water. After failure of a cathode lining, most of the metal and bath are tapped from the cell and materials remaining within the shell are removed. This "pot digging" op-

eration can be done either "wet" or "dry". In "wet digging", water is applied to the pot to shock thermally and to fracture the bath, metal, and lining material that remain in the pot.

The best approach to handling pot wash water is to minimize the amount of wastewater generated through good management practices during the soaking operation. Excess water is collected in a sump and used as makeup to the next pot brought in for relining. Under no circumstances is this water discharged to a receiving stream because it may contain cyanide (10–200 mg/L total CN⁻) and fluoride (100–600 mg/L).

Plant Runoff. Although aluminum smelting is a dry process, some water is required for services, such as boiler makeup, various equipment cooling needs, and area wash water. A major source of wastewater at a smelting plant is stormwater runoff. Although intermittent, the contaminant loading is significant if efforts are not made to keep courtyards relatively free of dust and to protect spent pot linings from the elements. To minimize the environmental impact of storm water and the other miscellaneous flows, many primary aluminum plants direct their storm sewers through an equalization/holding basin before discharge. This basin is designed to remove suspended solids and floating matter (oil and grease) and also to equalize the fluoride concentration.

21.7.3 Solid Waste

Eventually, the lining of an operating aluminum smelting pot, due to physical deterioration and both impregnation, either falls or needs to be replaced because of poor performance or metal quality. This lining, once removed from the pot, is known as "spent potlining" or SPL. SPL is the largest-volume solid waste generated by aluminum smelters, roughly 2% to 4% by weight of aluminum produced.

SPL consists of mostly carbon, sodium aluminum fluoride, and various compounds of aluminum, sodium, fluorides, and less than

1% cyanides. The heat value of SPL ranges from 5000 to 8000 BTU per pound. Grey to black in appearance, SPL is very hard and its size distribution is extreme: large chunks to very fine powder. It often has an ammonia odor.

The United States Environmental Protection Agency has listed SPL as a hazardous waste due to cyanide content. As of early 1997, U.S. regulations require treatment of SPL prior to land disposal. Other countries of the world regulate SPL or are considering such regulation.

After removal from the pot, SPL is temporarily stored in containers or piles inside buildings, protected from wind dispersal and precipitation. Typical treatment for SPL destroys the cyanides using thermal technology and renders the fluorides less soluble with chemical fixation or stabilization. Recycling options for SPL generally recover or use its heat or fluoride value. SPL has been used to manufacture cement, mineral wool, bricks, asphalt materials, and as flux in the steel industry. Research is continuing with goals to minimize SPL generation and further develop recycling options that are economical, technologically sound, and protective of the environment and health.

21.7.4 Regulatory Requirements

Regulatory limits throughout the world have been summarized in an International Primary Aluminum Institute publication [38]. In the United States new carbon bake furnace emissions are limited to 20% opacity and the total fluoride as a function of aluminum produced is set at 0.05 kg/t. New potroom emissions are limited to 10% opacity and 0.95 kg/t Al of Total Fluoride in the US by New Source Performance Standards. MACT (Maximum Achievable Control Technology) standards for existing sources regulate Total Fluoride for various sources from 0.95 to 1.5 kg/t Al (depending on source type) and also limit POM emissions from Söderberg reduction plants. MACT standards are also being set for new

and existing carbon baking furnaces and anode mixing and forming processes.

In the United States, effluent limitation guidelines have been promulgated for aluminum smelting that control toxic and other pollutants. These regulations are found in the Code of Federal Regulation, Title 40 — Protection of the Environment, Part 421, Subpart B — Primary Aluminum Smelting (40 CFR 421). Limitations are based on the level of production at each facility discharging wastewater. The pollutants regulated under the guidelines are benzo(a)pyrene, antimony, nickel, aluminum, fluoride, oil and grease, total suspended solids, and pH. The wastewater sources for which these limitations are applicable include:

- Anode and cathode paste plant wet air pollution control;
- Anode bake plant wet air pollution control;
- Cathode reprocessing;
- Anode and briquette contact cooling;
- Potline wet air pollution control;
- Potline SO₂ wet air pollution control;
- Potroom wet air pollution control;
- Pot repair and pot soaking.

21.8 Toxicology and Occupational Health

The American Conference of Governmental Industrial Hygienists continues to recommend a 10-mg/m³ TLV for aluminum metal and alumina dust, the same as for nuisance or biologically inert materials [39]. They also have established a lower limit applicable to aluminum pyro powder and aluminum welding fumes, 5 mg/m³. This concentration is consistent with limits for nuisance materials with particle sizes in the respirable range. Health regulatory agencies in Australia, Germany, the Netherlands, Sweden, and many other countries consider aluminum oxide dusts to be nuisance particulates [40]. No MAK values have been set.

The bulk of the epidemiologic literature confirms that, in humans, aluminum and its

compounds exhibit a very low order of toxicity [41–44]. Whether taken into the body by ingestion or by inhalation, very little aluminum finds its way into body tissues. The aluminum content of the adult human body is 50–150 mg [45, 46]. Because of its ubiquitous nature, aluminum also is found in many foods that make up our normal diets. The amount ingested ranges from as little as 1 to > 100 mg/d [47]. The use of aluminum cooking utensils and food packaging does not contribute significantly to the amount that is ingested normally [48, 49]. Regardless of the route of intake, most of the aluminum absorbed systemically is excreted in the urine.

For many years aluminum, in the form of Al(OH)₃, was used widely at high dosages as an antacid, with no apparent ill effects. Although aluminum is known to have neurotoxic properties [50–53], it does not exhibit these properties in normal human beings because it is eliminated readily from the body. On the other hand, for those who have impaired renal function, it can be neurotoxic. There are strong implications that aluminum is a major factor in dialysis encephalopathy, an ultimately fatal condition that sometimes occurs in those with renal failure who undergo dialysis. The major symptoms are speech difficulties, dementia, and seizures. Traces of aluminum in the water used for the preparation of dialysis fluid can accumulate in the patient because the impaired kidneys are unable to eliminate it.

Aluminum toxicity with neurologic effects has been reported in patients with renal insufficiency not receiving dialysis who chronically ingested aluminum-containing phosphate-binding gels [54]. Likewise, premature infants with immature renal systems have developed Al toxicity as a result of Al-rich IV infusions, formula, and medications [55, 56].

Those with renal failure, whose aluminum serum levels are elevated as a result of dialysis or the oral administration of aluminum compounds, are also at special risk of developing osteomalacia, a softening of the bone that re-

sults in pain and an increased incidence of bone fractures.

Although aluminum has been implicated as being associated with Alzheimer's disease, a condition of premature senility [57, 58], the evidence to date suggests that it is not causal. Aluminum's role, if it plays a part at all, appears to be secondary to some unknown primary agent [59, 60].

With a few exceptions, most of the literature dealing with inhalation exposures of humans and experimental animals to aluminum and its compounds shows these materials to be relatively innocuous. However, there are reports contending that aluminum and aluminum oxide dusts are fibrogenic. Critical examination of the original references reveals that the evidence for this contention is inconsistent and mitigated by compounding variables.

Cases of pulmonary fibrosis attributed to aluminum powder exposures have been reported in the literature [61–66]. In most of these instances, environmental conditions were poor, dust exposures were extremely high, materials other than aluminum were known or suspected to be present, smoking and work histories of those affected were not given, and the types of fibrosis seen were not always consistent. Of these cases, 47 in all, one was reported from Japan and the remainder from Europe. No case has been reported from North America, even though similar production operations were conducted there over the same period of time.

An unusual form of pulmonary fibrosis has been reported in workers exposed during the manufacture of fine aluminum dust ("pyropowder") used in explosives and pyrotechnics. First reported in Germany during and after World War II, it was later described in England [67–69] but has never been described in North America.

That disorder has been related to manufacturing methods in which aluminum powder is coated with a lubricant to prevent its spontaneous oxidation [70]. The traditional lubricant used for this purpose was stearic acid, a fatty acid which reacts with aluminum to form sta-

ble aluminum stearate. Less often, mineral oil was used.

Fibrosis developed only in those exposed to metallic aluminum coated with mineral oil [71, 72]. Unlike stearic acid, mineral oil does not react with aluminum and can be readily removed. Following inhalation, mineral oil-coated particles are ingested by alveolar macrophages which remove the mineral oil coating, allowing the aluminum to oxidize and cause pulmonary injury leading to pulmonary fibrosis [73, 74]. This particular lung disease has not been reported since methods of production changed more than 20 years ago.

A study of 125 employees involved in a powder stamping operation in the United States failed to show any evidence of fibrosis [75]. Their exposure times ranged from 6 to 23 years (mean average of 12). Furthermore, a therapeutic administration of heavy doses of aluminum powder, by inhalation, to silicotics over a period of 30–50 weeks showed no detrimental effects to the patients [75]. A report in 1973 indicated that the failure of inhaled metallic aluminum powder to cause pulmonary fibrosis in experimental animals "parallels the clinical experience in the United States but it leaves unexplained the occurrence of fatal pulmonary fibrosis in England from the inhalation of pyro aluminum powder" [76]. Worldwide, no case has been reported since 1962.

In 1947 cases of pulmonary fibrosis were attributed to aluminum oxide fume exposure [77]. Subsequent investigations demonstrated the presence of silica in these fumes [78]. Silica generally is accepted today as the principal cause.

Pulmonary exposure to nearly all forms of aluminum oxide (alumina) are without adverse effects [70, 79]. However, one specific transitional gamma form of alumina caused pulmonary fibrosis in animals after intratracheal injection, but not after inhalation [80–82]. That alumina is rarely encountered in aluminum production and has little relevance to occupational health concerns.

In humans, there is no systematic evidence that bauxite or alumina cause pulmonary fi-

brosis. Review of mortality experience for nearly 6000 aluminum smelter workers found no deaths due to fibrosis, although deaths from other respiratory diseases were increased [83]. Bauxite refinery workers had increased risk of obstructive pulmonary changes, consistent with industrial bronchitis from dust exposure, but the effect was less than that attributable to smoking [84, 85]. Moreover, none of the cross-sectional studies of aluminum smelter workers has found evidence of significant restrictive ventilatory defects, decreased pulmonary compliance or pneumoconiosis on chest x-ray [72].

21.9 Major Markets [86, 87]

By far the greatest part of aluminum shipments is in the form of aluminum alloys, and production of primary aluminum and consumption of aluminum are the best indicators of the importance of aluminum alloys.

World production of primary aluminum is summarized in Table 21.5, which shows average annual production for two five-year periods. In the interval between these periods, production increased in almost every country: the world increase exceeded 280%. In the latest period, the United States was the largest producer, with about 30% of the world total, followed by the former Soviet Union (12%), Canada (7%), Japan (6%), and West Germany (5%).

Per capita consumption of aluminum in selected countries is summarized in Table 21.6, which shows average annual per capita consumption for two five-year periods. Where data are available for both periods, consumption increased 1.3–7.0 times. For the latest period, the United States had the highest consumption, followed by Norway, West Germany, Japan, and Australia.

The major markets for aluminum products are shown in terms of use by major industries in the United States in Table 21.15. To eliminate duplication, the figures exclude intra-industry shipments for further fabrication.

Table 21.5: Average annual world primary aluminum production in kilotons.

Country	1978–1982	1960–1964
Argentina	116	—
Australia	316	33
Austria	93	73
Bahrain	135	—
Brazil	248	20
Cameroon	42	50
Canada	1034	667
China ^a	365	96
Czechoslovakia ^{ab}	37	53
Egypt	116	—
West Germany	732	189
France	409	285
East Germany ^a	61	48
Ghana	166	—
Greece	145	—
Hungary	73	53
Iceland	74	—
India	206	37
Iran	12	—
Italy	270	91
Japan	856	190
North Korea ^a	10	—
South Korea	19	—
Mexico	43	—
Netherlands	260	—
New Zealand	156	—
Norway	644	206
Poland ^c	80	43
Romania ^b	226	—
South Africa	85	—
Spain	324	41
Suriname	52	—
Sweden	82	19
Switzerland	83	51
Turkey	35	—
Taiwan	42	12
United Kingdom	332	32
United States	4266	1978
USSR ^a	1771	801
Venezuela	237	—
Yugoslavia	177	30

^a Estimated by the U.S. Bureau of Mines, Dept. of the Interior.

^b Includes secondary unalloyed ingot.

^c Includes primary alloyed ingot.

The weight shipped to the containers and packaging industry increased almost eightfold between the two periods, compared with increases of 1.5–2 for other industries. This is a striking shift in market distribution: containers and packaging moved from 7% to 24% of the market and is now the major market for aluminum products. This rapid growth reflects

the growth of the metal-can market, with aluminum capturing an ever-increasing share of that market. The impressive growth in shipments of aluminum sheet for cans is shown in Figure 21.14.

Table 21.6: Average annual per capita aluminum consumption (kg per person) in selected countries.

Country	1978-1982	1960-1964
Argentina	2.4	—
Australia	17.0	5.5
Austria	11.5	—
Bahrain	7.9	—
Belgium	8.7	3.4
Brazil	2.7	0.6
Cameroon	2.0	—
Canada	15.9	6.6
Denmark	14.5	—
El Salvador	0.3	—
Finland	7.4	—
West Germany	20.7	7.4
France	12.4	5.2
Greece	7.1	—
Iceland	9.9	2.5
Ireland	4.4	—
Italy	12.7	3.4
Japan	19.5	2.8
Mexico	2.4	—
Netherlands	11.0	2.7
New Zealand	8.1	—
Norway	21.8	6.7
Panama	0.9	0.3
Philippines	0.5	—
Saudi Arabia	8.7	—
Singapore	9.4	—
South Africa	3.6	—
Spain	5.6	1.3
Sweden	16.0	6.9
Switzerland	15.1	8.6
Taiwan	6.3	0.7
Turkey	1.1	—
United Kingdom	10.1	7.8
United States	26.9	13.8
Venezuela	5.8	1.2

21.10 Compounds

21.10.1 Aluminum Oxide

21.10.1.1 General Aspects

The first reference to an aluminum compound dates back to the fifth century B.C., when HERODOTUS mentioned alum. PLINY de-

scribed the use of "alumen" as a mordant around 80 A.D. The term alumina is probably derived from the word alumen. In 1754 MARGGRAF showed that a distinct compound existed in both alum and clays. GREVILLE (1798) described a mineral from India that had the composition Al_2O_3 and named it corundum, believing that this was the native name for this stone. HAÜY (1801) called a mineral "diaspore", whose composition, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, was determined by VAUQUELIN in 1802. Gibbsite was found by DEWEY in 1820; TORNEY (1822) showed this mineral to be $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The name hydrargillite was given to a similar mineral found later in the Ural Mountains. The latter term is used more widely outside the United States.

By X-ray diffraction, BÖHM and NICLASSEN [97] identified $\gamma\text{-AlO(OH)}$, later named böhmite (boehmite). BÖHM discovered a second type of Al(OH)_3 a year later. FRICKE [98] suggested the name bayerite for this material. Only a few, uncertain finds of natural bayerite have been mentioned in the literature [99]. VAN NORDSTRAND et al. [100] reported a third form of trihydroxide, which was later named nordstrandite in his honor.

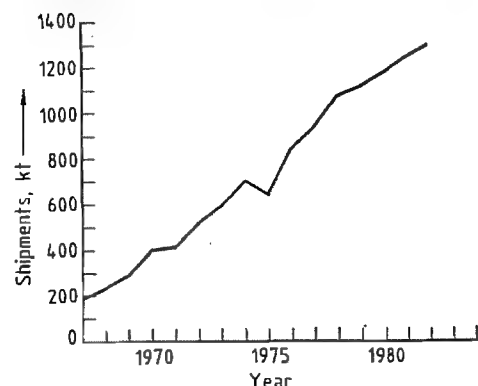


Figure 21.14: Shipments of aluminum sheet for cans.

Aluminum Hydroxides

A general classification of the various modifications of aluminum hydroxides is shown in Figure 21.15. The best defined *crystalline forms* are the three trihydroxides, Al(OH)_3 : gibbsite, bayerite, and nordstrandite. In addi-

tion two modifications of aluminum oxide hydroxide, AlO(OH) , exist: boehmite and diaspore. Besides these well-defined crystalline phases, several other forms have been described in the literature [89, 90]. However,

there is controversy as to whether they are truly new phases or simply forms with distorted lattices containing adsorbed or interlamellar water and impurities.

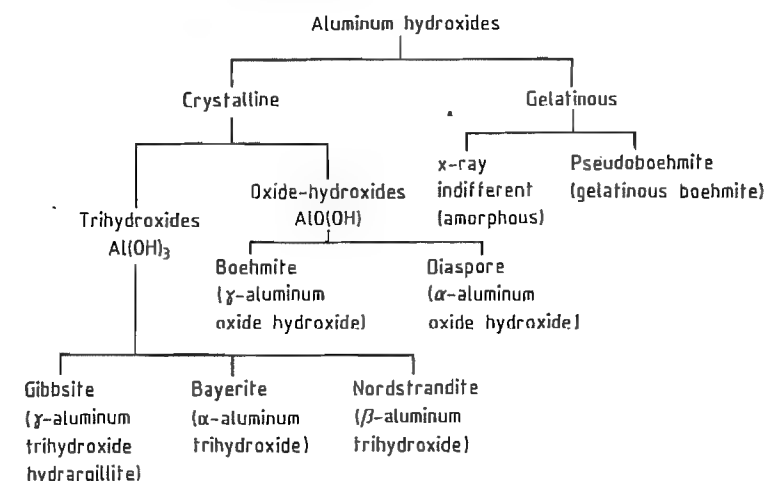


Figure 21.15: Classification of aluminum hydroxides (All figures courtesy of Aluminum Company of America).

Table 21.7: Mineralogical properties of oxides and hydroxides [90].

Phase	Refractive index n_D^{20}				Cleavage	Brittleness	Mohs hardness	Luster
	α	β	γ	Average				
Gibbsite	1.568	1.568	1.587	—	{001} perfect	tough	2.5 to 3.5	pearly vitreous
Bayerite	—	—	—	1.583	—	—	—	—
Boehmite	1.649	1.659	1.665	—	{010}	—	3.5 to 4	—
Diaspore	1.702	1.722	1.750	—	{010} perfect	brittle	6.5 to 7	brilliant pearly
	ϵ	ω	Average					
Corundum	1.7604	1.7686	—	none	tough when compact	9	pearly adamantine	

Table 21.8: Structural properties of oxides and hydroxides [90].

Phase	Formula	Crystal system	Space group	Molecules per unit cell	Unit axis length, $\times 10^{-1}$ mm			Angle	Density, g/cm ³
					a	b	c		
Gibbsite	Al(OH)_3	monoclinic	C_{2h}^5	4	8.68	5.07	9.72	94°34'	2.42
Gibbsite	Al(OH)_3	triclinic	—	16	17.33	10.08	9.73	94°10' 92°08' 90°0'	—
Bayerite	Al(OH)_3	monoclinic	C_{2h}^5	2	5.06	8.67	4.71	90°16'	2.53
Nordstrandite	Al(OH)_3	triclinic	C_i^1	4	98.75	5.07	10.24	109°20' 97°40' 88°20'	—
Boehmite	AlO(OH)	orthorhombic	D_{2h}^{17}	2	2.868	12.227	3.700	—	3.01
Diaspore	AlO(OH)	orthorhombic	D_{2h}^{16}	2	4.396	9.426	2.844	—	3.44
Corundum	Al_2O_3	hexagonal (rhomb.)	D_{3d}^6	2	4.758	—	12.991	—	3.98

Gelatinous hydroxides may consist of predominantly X-ray indifferent aluminum hydroxide or pseudoboehmite. The X-ray diffraction pattern of the latter shows broad bands that coincide with strong reflections of the well-crystallized oxide hydroxide boehmite.

Identification of the different hydroxides and oxides is best carried out by X-ray diffraction methods [90]. Mineralogical and structural data are listed in Tables 21.7 and 21.8.

The aluminum hydroxides found abundantly in nature are gibbsite, boehmite, and diasporite. *Gibbsite* and *bayerite* have similar structures. Their lattices are built of layers of anion octahedra in which aluminum occupies two thirds of the octahedral interstices. In the gibbsite structure, the layers are somewhat displaced relative to one another in the direction of the *a* axis. The hexagonal symmetry of this lattice type (brucite type) is lowered to monoclinic. Triclinic symmetry was found in larger gibbsite single crystals from the Ural Mountains [101]. This investigation revealed that the layer packets were slightly shifted in the direction of the *b* axis as well.

In bayerite the layers are arranged in approximately hexagonally close packing. Because of shorter distances between the layers, the density is higher than in the case of gibbsite. The crystal class and space group of bayerite have not yet been established clearly.

The individual layers of hydroxyl ion octahedra in both the gibbsite and the bayerite structure are linked to one another through weak hydrogen bonds only. Bayerite does not form large single crystals. The most commonly observed growth forms are spindle- or hourglass-shaped somatoids. The long axis of these somatoids stands normal to the basal plane, i.e., the somatoids consist of stacks of $\text{Al}(\text{OH})_3$ layers (Figure 21.16). The effect of alkali ions on the structures of $\text{Al}(\text{OH})_3$ types was investigated by several workers [90, 102, 103].

Gibbsite crystals of appreciable size are not uncommon. Clear pseudohexagonal platelets about 1 mm in diameter are known from Aro in Norway. Prismatic crystals of 0.5–1 mm

length are occasionally produced in the Bayer process.

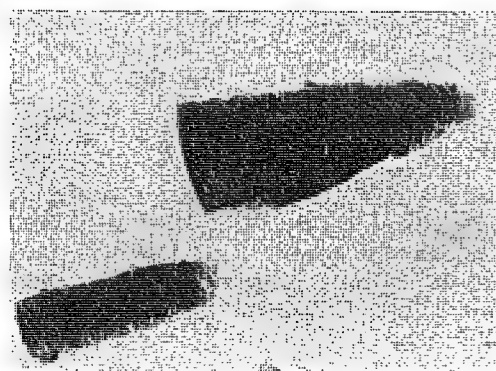


Figure 21.16: Somatoids of bayerite.

Nordstrandite, the third form of $\text{Al}(\text{OH})_3$, was described by VAN NORDSTRAND [100] and others [104]. The structures of nordstrandite and bayerite were investigated [105] and compared with those of the monoclinic and triclinic gibbsite, which had been determined previously [101].

The lattice of nordstrandite is built of the same, electrically neutral $\text{Al}(\text{OH})_3$ octahedral layers that form the structural elements of gibbsite and bayerite [98]. The lattice period amounts to 1.911 nm in the direction of the normal to the layer. This corresponds to the sum of identical layer distances of bayerite plus gibbsite. The ideal nordstrandite structure consists of alternating double layers, in which the OH octahedra are arranged once in the packing sequence of bayerite, and then in that of gibbsite. Material containing continuous transitions from bayerite via nordstrandite to gibbsite has been prepared through the proper selection of precipitation conditions [102].

Tucanite, which contains about 0.5% SiO_2 , has the composition $\text{Al}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ [106]. Preliminary X-ray diffraction data show a resemblance of the tucanite structure to triclinic gibbsite. Yet, the layer spacing seems to be somewhat larger than in triclinic and monoclinic $\gamma\text{-Al}(\text{OH})_3$. Incorporated water molecules may be the cause of this.

A similar influence of water molecules on layer spacing has been observed in the oxide hydroxide boehmite [105].

Pseudoboehmite is formed during aging of X-ray indifferent hydroxide gels as a precursor of trihydroxide. The reflexes of pseudoboehmite are broadened not only because of the very small particle size, but also because of variable distances of the $\text{AlO}(\text{OH})$ double chains, which form the structural element of pseudoboehmite as well as of well-crystallized $\gamma\text{-AlO}(\text{OH})$. The lattice spacing in the direction of the *c* axis increases by 0.117 nm for each mole of excess water [105].

Aluminum Oxide Hydroxides

The $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ System. Under the equilibrium vapor pressure of water, crystalline $\text{Al}(\text{OH})_3$ converts to $\text{AlO}(\text{OH})$ at about 375 K. The conversion temperature appears to be the same for all three forms of $\text{Al}(\text{OH})_3$. At temperatures lower than 575 K, boehmite is the prevailing $\text{AlO}(\text{OH})$ modification, unless diasporite seed is present. Spontaneous nucleation of diasporite requires temperatures in excess of 575 K and pressures higher than 20 MPa. In the older literature, therefore, diasporite was considered the high-temperature form of $\text{AlO}(\text{OH})$. The first reaction diagram of the phase transitions in the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system was published in 1943 [107]. These workers determined the gibbsite \rightarrow boehmite conversion temperature to be 428 K. Boehmite transformed to diasporite above 550 K; diasporite converted to corundum, $\alpha\text{-Al}_2\text{O}_3$, at 725 K. Similar results were reported in 1951 [108].

The system was reinvestigated in 1959 [109] and in 1965 [110]. A phase diagram based on these data is shown in Figure 21.17. Diasporite is the stable modification of $\text{AlO}(\text{OH})$; boehmite is considered metastable, although it is kinetically favored at lower temperatures and pressures. This is because the nucleation energy is lower for boehmite than for the considerably more dense diasporite. In addition, $\gamma\text{-Al}(\text{OH})_3$ and $\gamma\text{-AlO}(\text{OH})$ have similar structures. Nucleation is, therefore, additionally facilitated by the possibility that boehmite can grow epitaxially on $\text{Al}(\text{OH})_3$. In the $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-H}_2\text{O}$ system, the presence of

the isostructural goethite, $\alpha\text{-FeO}(\text{OH})$, lowers the nucleation energy for diasporite so that this $\text{AlO}(\text{OH})$ modification crystallizes at temperatures near 373 K [111]. This observation explains the occurrence of diasporite in clays and bauxite deposits that have never been subjected to high temperatures or pressures.

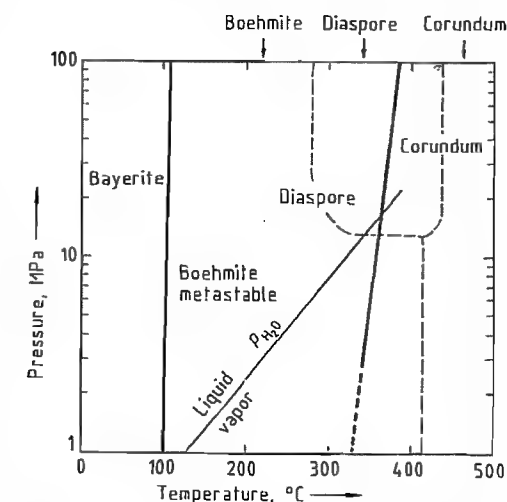


Figure 21.17: The $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system. Dashed lines [108], solid lines [109, 110].

Structure. Boehmite consists of O, OH double layers in which the anions are in cubic packing. The aluminum ions are octahedrally coordinated. These layers are composed of chains of $[\text{AlO}(\text{OH})]_2$ extending in the direction of the *a* axis [112]. The double layers are linked by hydrogen bonds between hydroxyl ions in adjacent planes. Boehmite crystals exhibit perfect cleavage parallel to the (010) plane.

In the diasporite structure the oxygen ions are nearly equivalent, each being joined to another oxygen through a hydrogen ion. The anions are hexagonally close packed [113]. The position of the hydrogen ion has been established by neutron diffraction [114]. The O–H–O distance is 0.265 nm.

By infrared studies, the bond energy for the hydrogen bridges in diasporite was determined to be 28.7 kJ/mol, compared with 20.1 kJ/mol for boehmite [115].

Nomenclature. Although there is fairly good agreement in the more recent literature on phase fields and structures of the crystalline phases in the $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$ system, the nomenclature is still rather unsystematic.

Bayerite, gibbsite (hydrargillite), and nordstrandite are trihydroxides of aluminum, and not oxide hydrates. The designation "aluminum oxide monohydrate" for boehmite and diasporite is also incorrect. Both are true oxide hydroxides. Molecular water has been determined in poorly crystallized, non-stoichiometric pseudoboehmite only.

The sodium ions have been removed from the lattice of the so-called β -alumina, $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, by leaching with H_2SO_4 , and the ions replaced with H_2O molecules [117]. This is to date the only case in which the existence and structure of an alumina hydrate have been confirmed. As an intercalation compound, however, this hydrate has no phase field in the $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$ system.

The designation of the modifications of aluminum hydroxides and oxides lacks uniformity just as much as does the nomenclature of the compounds. According to the general usage in crystallography, the most densely packed structures are designated as α -modifications [90]. Bayerite, diasporite, and corundum fall within this class. The compounds with cubic packing sequence, gibbsite and boehmite, have been designated by the symbol γ . Nordstrandite can be classified as β - $\text{Al}(\text{OH})_3$ when regarding this compound not as an intergrowth of bayerite and gibbsite, but as an independent modification.

Aluminum Oxide, Corundum

The hexagonally closest packed α - Al_2O_3 modification is the only stable oxide in the $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$ system. Corundum is a common mineral in igneous and metamorphic rocks. Red and blue varieties of gem quality are called ruby and sapphire, respectively. The lattice of corundum is composed of hexagonally closest packed oxygen ions forming layers parallel to the $\langle 0001 \rangle$ plane. Only two thirds of the octahedral interstices are occupied by alu-

minum ions. The structure may be described roughly as consisting of alternating layers of Al and O ions. The corundum structure was determined in the early 1920s [118]; numerous workers later confirmed and refined these data [90]. Properties of corundum are listed in Tables 21.7 and 21.8.

Thermal Decomposition of Aluminum Hydroxides

When aluminum hydroxides or oxide hydroxides are heated in air at atmospheric pressure, they undergo a series of compositional and structural changes before ultimately being converted to α - Al_2O_3 . These thermal transformations are topotactic. Despite a loss of 34 or 15% of mass for the trihydroxides or oxide hydroxides, respectively, the habit of the primary crystals and crystal aggregates changes very little. This leads to considerable internal porosity, which may increase the specific surface area of the material to several hundred m^2/g . Structural forms develop that, although not thermodynamically stable, are well reproducible and characteristic for a given temperature range and starting material. These transition aluminas have been the subject of numerous investigations because of their surface activity, sorptive capacity, and usefulness in heterogeneous catalysis. The literature in this field of physical chemistry has been reviewed up to 1972 [90].

The simplest transformation is that of diasporite to corundum. As the structures of these two compounds are very similar, the nucleation of α - Al_2O_3 requires only minor rearrangement of the oxygen lattice after the hydrogen bonds are broken. A temperature below 860–870 K is sufficient for complete conversion. The newly formed corundum grows epitaxially on the decomposing diasporite, with the $\langle 0001 \rangle$ plane of Al_2O_3 parallel to the $\langle 010 \rangle$ plane of $\text{AlO}(\text{OH})$ [119].

The thermal transformation, at ambient pressure, of α - $\text{AlO}(\text{OH})$ and the trihydroxides to α - Al_2O_3 requires considerably more structural rearrangements and is generally not completed until the temperature reaches at least

1375–1400 K. The first step in the reaction sequence is the diffusion of protons to adjacent OH groups and the subsequent formation of water [120, 121]. This process begins at a temperature near 475 K. If this water cannot diffuse rapidly out of larger trihydroxide particles, hydrothermal conditions may develop locally, resulting in the formation of γ - $\text{AlO}(\text{OH})$. With increasing loss of water, a large internal porosity develops. The lattice voids left by the escaping water are not readily healed because of the slow diffusion in this low temperature range. The voids are oriented parallel and perpendicular to the basal plane of the trihydroxide crystals (Figure 21.18).

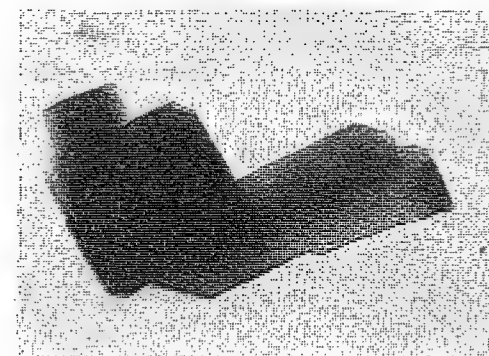


Figure 21.18: Gibbsite heated to 573 K.

The highest surface area and lowest crystalline order of the solid (not counting newly formed boehmite) is obtained at a temperature around 675 K. With increasing temperature the surface area decreases, while the density of the solid shows progressively higher values (Figure 21.19). This trend is the result of progressive reordering and consolidation of the solid.

During the thermally activated consolidation and reordering, the solid goes through structural stages that are influenced by the nature of the starting material as well as by heating rates, furnace atmosphere, and impurities. The general reaction paths are illustrated in Figure 21.20.

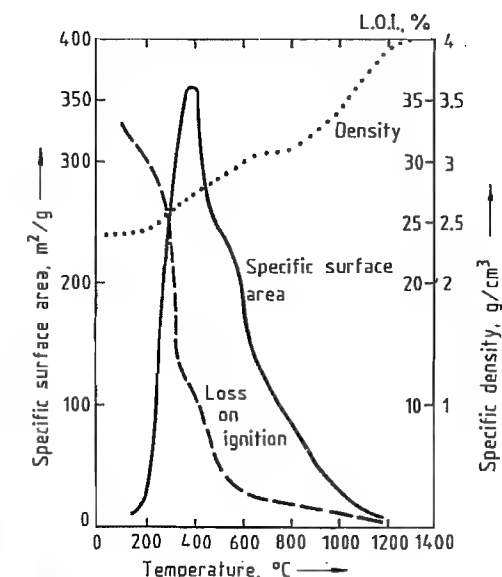


Figure 21.19: Specific surface area, loss on ignition (LOI), and density of heated $\text{Al}(\text{OH})_3$.

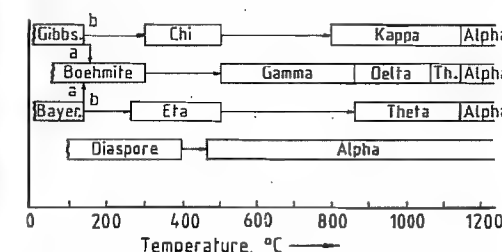


Figure 21.20: Decomposition sequence of aluminum hydroxide.

Transition oxides formed at lower temperatures are mostly two-dimensionally, short-range ordered domains within the texture of the decomposed hydroxides. Extensive three-dimensional ordering begins at about 1050 K. Until completely converted to corundum, the solid retains considerable amounts of OH^- ions. Most likely protons are retained to maintain electroneutrality in areas deficient of cations. The presence of protons therefore may retard the reordering of the cation sublattice. Addition of fluorine to the furnace atmosphere removes protons. As a result, rapid transition to α - Al_2O_3 occurs at temperatures as low as 1150 K. Markedly tabular corundum crystals form, possibly because the preceding transi-

tion alumina is mostly two-dimensionally ordered [122].

Transition forms other than the ones shown in Figure 21.20 can be obtained by hydrothermal treatment [90]. The structures of various transition forms have been investigated [123, 101, 105].

Aluminates and Related Compounds

Sodium oxide forms several compounds with aluminum oxide. These so-called β -aluminas represent a group of aluminates having the same, or very similar, structures but variable chemical composition. Their molar ratios ($\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$) can vary between 1:1 and 1:11. The 1:1 sodium aluminate, NaAlO_2 , exists in at least two allotropic modifications. Orthorhombic β - NaAlO_2 is stable below 750 K; the higher-temperature γ modification is tetragonal. For preparation and properties of technical sodium aluminate, see Section 21.10.3.1.

The 1:11 β - Al_2O_3 crystallizes from melts containing aluminum oxide and sodium oxide or other sodium compounds. A 1:5 β -alumina has been prepared by heating α - Al_2O_3 with NaAlO_2 or Na_2CO_3 at about 1325 K.

Several other β -aluminas containing CaO , BaO , or SrO in 1:6 ratio also have been reported [90].

Recent interest in β -alumina is related to its use as a solid electrolyte in sodium sulfur secondary batteries.

21.10.1.2 Bauxite, the Principal Raw Material

Definition and Geology

The term bauxite is used for sedimentary rocks that contain economically recoverable quantities of the aluminum minerals gibbsite, boehmite, and diaspore. The name derives from the description by BERTHIER, in 1821, of a sediment that occurred near the village of Les Baux in the Provence, France. Originally assumed to be a dihydrate of aluminum oxide, bauxite was later recognized to be composed of aluminum hydroxide, iron oxide and hy-

droxide, titanium dioxide, and aluminosilicate minerals [89].

Early in this century, major bauxite deposits were found in various parts of the Tertiary and Cretaceous limestone formations of the European Alpidic mountains; also in several locations on the North American continent, e.g., in Arkansas, Alabama, and Georgia. Since the 1920s, extensive deposits have been discovered in the tropical and subtropical climate belts.

The oldest known bauxites developed in the Precambrian; the youngest are of recent origin. Deposits may occur as extensive, flat bodies blanketing areas of many square miles; they may form irregularly shaped fillings of dolinas in old karst surfaces, or lenses several hundred meters in diameter and tens of meters thick. Allochthonous, i.e., displaced bauxites, are also common; erosion of primary deposits and redeposition of the detritus in valleys or along mountain slopes has frequently led to mineable accumulations of ore.

Many of the geologically younger bauxites are covered only by thin layers of soil; others are buried by coastal or alluvial sediments. Older deposits, especially in the Balkans or the Ural Mountains, often are overlain by carbonate rocks hundreds of meters thick. Regardless of their geologic age, all bauxites were formed during continental periods [124].

Composition and Properties

The chemical composition of bauxites of various origin is given in Table 21.9 [89]. Aluminum oxide, iron oxide, and titanium and silicon dioxides are the major chemical components of all bauxites. Alkali and alkaline earth compounds are rarely found.

Gibbsite, γ - $\text{Al}(\text{OH})_3$, is the predominant aluminum mineral in the geologically young bauxites of the tropical climate belt. Mesozoic and older bauxite contain mostly boehmite (γ - $\text{AlO}(\text{OH})$) or diaspore (α - $\text{AlO}(\text{OH})$). Since their formation, many of the older bauxites have been buried under considerable layers of younger sediments and often were subjected to tectonic stress. Boehmite and diaspore for-

mation appears to be related to an increasing degree of metamorphism. However both minerals also occur in young deposits, although in minor quantities. The chemical environment obviously plays as important a role in the formation of boehmite and diaspore as do pressure and stress [124].

Table 21.9: Principal chemical constituents of various bauxites, %.

Country and location	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Loss on ignition
Australia					
Darling Range	37	26.5	16.4	1.1	19.3
Weipa	58	4.5	6.9	2.5	26.8
Brazil					
Trombetas	52	5.1	13.9	1.2	28.1
France					
Southern districts	57	4.6	22.6	2.9	15.1
Guyana					
Mackenzie	59	4.9	2.9	2.4	30.4
Guinea					
Friguia	49	6.1	14.2	1.6	28.1
Boké	56	1.5	7.9	3.7	30.1
Hungary					
Halimba	52	6.6	23.5	2.9	18.1
India					
Orissa	46	2.7	22.4	1.1	24.2
Indonesia					
Bintan	53.5	3.9	12.1	1.6	29.2
Jamaica					
Clarendon	47.8	2.6	17.6	2.3	27.3
Suriname					
Onverdacht	59	4.3	3.1	2.5	30.9
Moengo	54	4.2	10.4	2.8	28.9
United States					
Arkansas	51	11.2	6.6	2.2	28.4
Former USSR					
Severouralsk	54	6.2	14.8	2.4	15.7
Former Yugoslavia					
Mostar	52	3.9	21.2	2.7	16.2

Dissolution of gibbsite requires the mildest conditions in the Bayer process. Higher temperatures and alkali concentrations are necessary for the digestion of boehmite and diaspore. Technically, both oxide hydroxides can be processed without difficulties. The current abundance of high-grade gibbsitic bauxites, however, has made boehmite- and diaspore-rich ores economically less attractive.

Goethite, α - $\text{FeO}(\text{OH})$, and hematite, α - Fe_2O_3 , are the most prevalent iron minerals in

bauxites. They are practically inert under the conditions of the Bayer process. In both minerals, some of the iron may be replaced isomorphically by aluminum ions. This amount of aluminum is included in the chemical analysis of the bauxite but is normally not extracted in the digest. Magnetite (Fe_3O_4) is found in some European bauxites; pyrite (FeS_2) and siderite (FeCO_3) also may occur. Decomposition of pyrite may lead to high sulfur levels in the process solutions.

Anatase, TiO_2 , is the titanium mineral found most frequently in bauxites. Rutile, TiO_2 , occurs in some European deposits; FeTiO_3 is also present in minor quantities, especially in titanium-rich bauxites. Titanium dioxide minerals are attacked under only the most severe conditions of the Bayer process.

Silicon dioxide may occur as quartz, as in the bauxites of the Darling Range in Western Australia. Most commonly, however, SiO_2 is associated with the clay minerals kaolinite, halloysite, or montmorillonite. These aluminosilicates react with sodium aluminate solutions to form insoluble sodium aluminum silicates during digest, causing loss of sodium hydroxide and extractable alumina. The amount of the so-called reactive silica is one of the major factors determining quality and price of the ore.

Minor constituents, such as chromium, vanadium, zinc, and gallium, have little effect on the Bayer process or on the quality of the final product. Some tend to accumulate in the circulated process solutions (e.g., gallium and vanadium) and must be removed periodically by appropriate treatments.

The physical properties of bauxites, i.e., texture, hardness, and density, can vary widely. Geologically old diaspore bauxites, especially those high in iron oxide, are very hard and can reach densities of 3.6 g/cm^3 . Young tropical deposits, in contrast, may have an earthy, soft texture and a density around $2.0\text{--}2.5 \text{ g/cm}^3$. Allochthonous bauxite often consists of hard nodules embedded in a soft, usually clayey matrix. Porous textures also occur. The color of bauxites is largely determined by the type and particle size of the

prevalent iron mineral. Highly dispersed goethite tends to be yellow to orange, whereas dark brown tones usually are associated with coarser hematite. Colors can vary greatly within a single ore body.

Hardness, texture, and the amount of overburden determine the methods applied for bauxite mining. Deposits in Greece, former Yugoslavia, Hungary, and former USSR require deep mining to depths of several hundred meters, often complicated by the difficulties of controlling water levels in the porous limestone formations. Tropical bauxites frequently are located so close to the surface that they can be recovered with normal earth-moving equipment.

Genesis of Bauxites

Many of the geologically young bauxite deposits are located in the savannah region, which extends north and south of the tropical rain forest belt. The climate of this region is characterized by a high mean annual temperature and abundant precipitation during the rainy season. Deposits occur on gently sloping hills or on peneplains. The stratigraphic evidence shows that these bauxites have formed in situ. Parent rocks may be coarse-grained, igneous rocks such as syenite, phonolite, basalt, or gabbro. However, large deposits also developed on kaolinitic sandstones, on phyllites, and on schists. A layer of kaolinitic clay is frequently found between the ore body and the parent rock.

Bauxite probably forms during long periods of low geologic activity when the combination of high temperature, abundant precipitation, and good vertical drainage favors intensive chemical weathering. The sequence of leaching begins with removal of alkali followed by the removal of alkaline earths. Oxides of iron, aluminum, titanium, and silicon are mobilized and reprecipitated as hydroxides and oxides. Aluminum hydroxide and silica form kaolinite, $\text{Al}_4(\text{OH})_8\text{Si}_4\text{O}_{10}$. This sequence first leads to the formation of tropical soils (laterites). Bauxitization follows when the climatic, chemical, and topographic

conditions prevail long enough to allow the removal of silicon dioxide as well.

The bauxite deposits of the Mediterranean region, the Caribbean Islands, and many other locations that are associated with tertiary and older limestone formations (karst bauxites) were formed by a similar weathering process. Parent materials were lateritic soils and clays transported into the karst region and deposited in depressions. During extended terrestrial periods, high mean temperatures, copious precipitation, and good vertical draining through the porous limestone bedrock facilitated a thorough desilification. In the older literature, the parent material for karst bauxitization was reported to be clayey residue left after weathering of substantial layers of carbonate rocks [125]. Researchers have shown conclusively that igneous rocks were the source of this material [126–128].

Comprehensive reviews of the geology, mineralogy, and genesis of bauxites have been given [124, 129].

Table 21.10: World bauxite reserves and production, $\times 10^3$ t [130].

Country	Mine production		Reserve base
	1982	1983	
Australia	23 621	23 000	4 600 000
Brazil	4 186	3 900	2 300 000
Greece	2 853	3 100	650 000
Guinea	10 908	9 000	5 900 000
Guyana	953	800	900 000
Hungary	2 627	2 800	300 000
India	1 854	2 000	1 200 000
Jamaica	8 380	7 400	2 000 000
Suriname	3 059	2 700	600 000
United States	732	700	40 000
Former USSR	4 600	4 600	300 000
Former Yugoslavia	3 668	3 600	400 000
Other market economy countries	4 820	5 000	3 100 000
Other centrally planned countries	2 180	2 300	200 000
World total (rounded)	74 441	71 000	22 500 000

Major Bauxite Deposits

Until the 1950s, the European aluminum industry was supplied from the karst bauxite deposits of France, Hungary, Yugoslavia, and Greece. United States sources (Arkansas) and ore from Suriname provided the raw material

for North American production. Since then, the picture has changed drastically. The four largest bauxite producers of 1982, namely, Australia, Guinea, Jamaica, and Brazil (Table 4) [130], hardly would have been mentioned in 1950. Today, they provide more than half of the world's total bauxite output (even at the depressed levels shown for 1982, which are more than 10^7 t lower than the production in 1981).

Africa. The savannah region covers an area of the African continent that has experienced low geologic activity for a long time. In this belt, which stretches from the Ivory Coast to Madagascar, very large bauxite deposits were found. The major production is currently concentrated in Guinea and Ghana. Cameroon, Sierra Leone, Mali, and the Congo region, among other areas, have substantial reserves.

Australia. Major deposits are located in the Darling Range in Western Australia, on the Gove Peninsula in the Northern Territory, and on the Cape York Peninsula in Queensland. Bauxite also occurs in New South Wales, in Victoria, and on the island of Tasmania. The Australian deposits developed between the Eocene and Pliocene epochs on substrates ranging from Precambrian sandstones to Tertiary basalts. Gibbsite is the predominant aluminum mineral, although some boehmite occurs in all but the Western Australian deposits.

South America. On the outer slopes of the old Guyana Shield, many economically important deposits have been found. They are located in the Amazon Basin of Brazil, in Colombia, Venezuela, Suriname, Guyana, and French Guyana. Suriname and Guyana have been producing for more than 60 years, whereas the Brazilian Amazon deposits have been mined only recently. Bauxite also is produced in the Pocos de Caldas area in Southern Brazil, state of Minas Gerais. The South American bauxites generally are geologically young, gibbsitic ores.

Caribbean. Jamaica and the Dominican Republic have major reserves of karst bauxites that occur on Tertiary limestones under generally very thin overburden. Although gibbsite

is the main aluminum mineral, some boehmite also is present. Jamaica has been one of the world's leading bauxite producers for the past 20 years.

North America. The only economically important deposit is located in Arkansas, where gibbsitic bauxite developed on nepheline syenite during the Eocene. Less than 5×10^7 t of bauxite remain, and the grade is declining.

Europe. Except for a few commercially insignificant occurrences, all European bauxites are of the karst type. The oldest deposits (Devonian/Mississippian) are those of the Tikhvin area in the USSR; the youngest are the Eocene bauxites of Yugoslavia. Most European deposits developed during the Lower and Upper Cretaceous, e.g., the diasporite and boehmite bauxites of France, Greece, and Romania, and the gibbsite and boehmite bauxites found in Hungary, Yugoslavia, and Italy. Today, all European mines combined contribute only about 17% of world production.

Asia. Major deposits of gibbsite bauxites occur in India; the island of Kilimantan (Indonesia) has large potential reserves. Numerous bauxite deposits, most of them containing geologically old, diasporite-rich ore, were found in China. Substantial deposits also are located in Western Siberia.

Economic Aspects

The proved reserves of bauxite shown in Table 21.10 are sufficient to supply the world aluminum industry for a few centuries. Total resources are estimated by the U.S. Geological Survey at 40 to 50×10^9 t. Because of the worldwide distribution of significant ore deposits, a disruption of bauxite supply for political reasons appears highly unlikely. In 1974 several major bauxite-producing nations formed the International Bauxite Association (IBA) with the intent of increasing control over the exploitation of their bauxite deposits. Although levies were increased substantially, competition from countries not associated with the IBA helped maintain a reasonable price structure.

Economic and political considerations currently favor refining of bauxite near the deposit and shipment of either alumina or aluminum ingot. Brazil, Suriname, and Australia have smelters, although their refining capacity by far exceeds the demands of domestic metal production. Jamaica and Guinea refine a substantial portion of their own bauxite production.

About 25% of all bauxite mined is used for producing abrasives, catalysts, adsorbents, and other industrial chemicals.

21.10.1.3 Bayer Process

History and Procedure

Pure Al_2O_3 became the raw material for aluminum production upon development of the Hall-Héroult cell. The first alumina was prepared by thermal decomposition of aluminum salts and by sintering bauxite with soda (LE CHÂTELIER). This changed when in 1887 the Austrian chemist, KARL JOSEF BAYER, developed the process that bears his name. His first work was done in an experimental plant in Russia. Construction of the first large commercial Bayer plant was begun in 1901 in East St. Louis, Illinois. Since that beginning, plants have been built in at least 25 countries, and the present world capacity is over 4×10^7 t/a [88-93].

The important features exploited in the Bayer process are that boehmite, gibbsite, and diasporite can be dissolved in NaOH solutions under moderate conditions; the solubility of Al_2O_3 in NaOH is temperature dependent; most other components of the bauxite are quite inert in the process; and the silica that does dissolve subsequently forms a nearly insoluble compound. These features permit formation of a sodium aluminate solution, physical separation of the impurities, and precipitation of pure $\text{Al}(\text{OH})_3$ from the cooled solution.

Figure 21.21 shows the flow sheet of the process as it is now practiced.

Each operation in the process is carried out in a variety of ways. The process begins with

preparation of the bauxite by blending for uniform composition followed by grinding. In most plants the bauxite is ground while suspended in a portion of the process solution. This slurry is mixed with the balance of the heated NaOH solution, then treated in a digester vessel at well above atmospheric pressure. The digest reaction is:



Additional reactions convert impurities such as SiO_2 , P_2O_5 , and CO_2 to relatively insoluble compounds. The other bauxite constituents remain as solids. The slurry leaves the digester at a temperature above its atmospheric boiling point and is cooled by flashing off steam as the pressure is reduced in several stages. The flashed steam is used to heat the slurry and the solution going to the digester. The bauxite residue solids are separated from the sodium aluminate solution in two steps so that the coarse fraction is processed separately from the fine. Both residue fractions are washed and discarded. The solution, being free of solids, is cooled and seeded with fine crystals of $\text{Al}(\text{OH})_3$; this causes the $\text{Al}(\text{OH})_4^-$ ions to decompose to $\text{Al}(\text{OH})_3$, thereby reversing the reaction that previously had taken place in the digester. Again, the heat removed in cooling the solution is used to heat a colder stream in the process. After the precipitation reaction has proceeded to the point that about half of the Al_2O_3 in the solution has been removed, the mixture of solids and solution is sent to classifiers. The fine $\text{Al}(\text{OH})_3$ particles are returned to the process to serve as seed. The coarse particles are washed and calcined to Al_2O_3 . Excess solution introduced in washing the product and the residue must be removed by evaporation. In some cases the solution is treated to remove both organic and inorganic impurities before the solution is recycled through the plant.

Bauxite Preparation

The bauxite entering the refinery must be uniform and sufficiently fine that extraction of the Al_2O_3 and that the other operations are successful. The chemical composition of

bauxite varies. Uniformity is improved by blending material mined from several pits and, if necessary, by adding bauxite from storage piles. A more recent development is to store ground bauxite slurry in surge tanks before it is pumped to digestion. These agitated tanks are operated so that plant feed is uniformly blended for several hours. Sometimes bauxites are dried to improve handling or washed to remove clay.

Hard bauxite is reduced to particles finer than 2 cm in roll or cone crushers and hammermills. Before it enters the process it is ground further to less than 0.15 cm.

Previously, fine grinding was done in dry mills operating in closed circuit with vibrating screens. Such operation required very dry bauxite to avoid blinding the screens. This resulted in a dusty working environment. In most modern plants, the bauxite is mixed with a portion of the process solution and is ground as a slurry. Rod mills and ball mills are used most frequently. The ground slurry may be passed over screens or through cyclones, with the fine particles progressing and the coarse ones being returned to the mills.

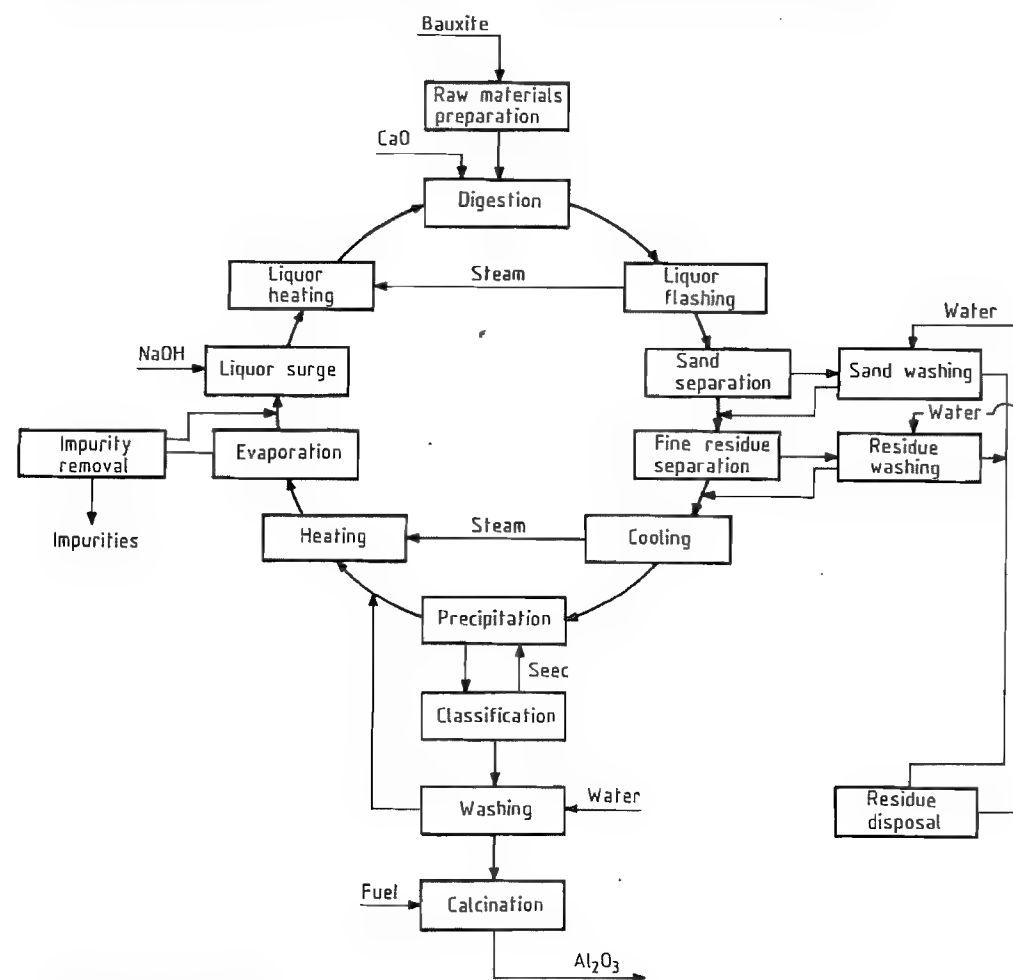


Figure 21.21: Bayer process flow sheet.

In all-wet grinding the bauxite feed and the flow of solution are controlled to keep the solids content of the slurry between 45 and 55%. The power consumed by the mill drive is an indicator of the amount of grinding being done and may be used to control the feed to the mill. On a longer time scale the particle size of the product can be used to make changes in the grinding operation.

Digestion

In digestion, all of the Al_2O_3 in the bauxite must be extracted. A solution is produced that contains the maximum Al_2O_3 concentration that can remain stable through the rest of the process. This must be accomplished while using a minimum amount of energy.

The conditions for digestion can and do vary widely. The first consideration is whether the available Al_2O_3 is present as gibbsite, boehmite, diaspor, or a mixture of these minerals. The dissolution rates of the three are quite different. Generally, if the bauxite contains mixed phases, the digestion conditions will be chosen on the basis of the least soluble compound. Any $\text{Al}(\text{OH})_3$ or AlOOH left undissolved can act as seed in the clarification step, causing precipitation of $\text{Al}(\text{OH})_3$ while the residue is still in contact with the solution. In the sweetening process, boehmitic bauxite is digested under relatively mild conditions, producing an intermediate Al_2O_3 concentration. In a separate vessel, gibbsitic bauxite is added to the flow from the first digest to raise the Al_2O_3 concentration to the desired level. Another approach is to digest only the gibbsite in a mixed bauxite. The residue is separated from the solution and redigested under more severe conditions to recover the boehmite. This method reduces the flow to the high-temperature digest and so requires lower capital and operating costs.

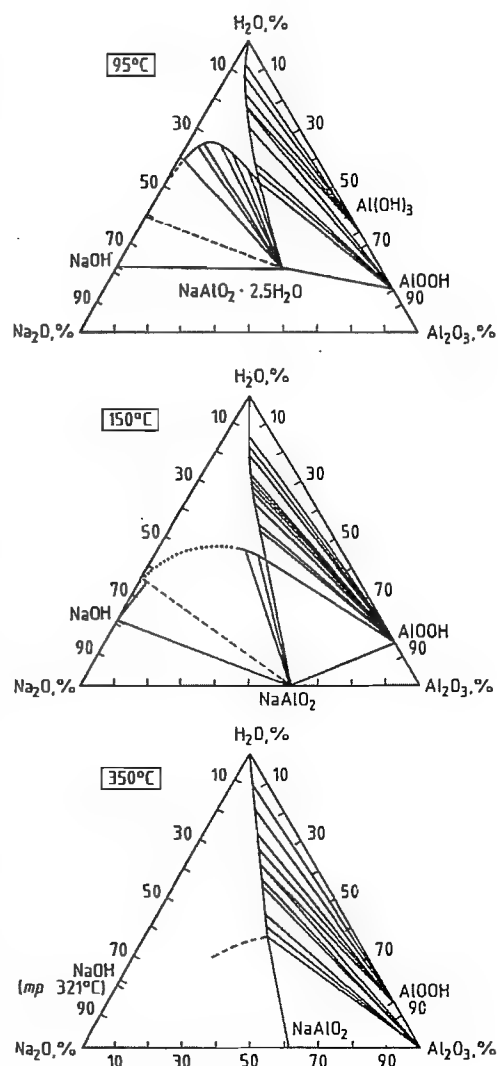


Figure 21.22: Phase diagram $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$.

The solubility data (Figure 21.22) show that the Al_2O_3 concentration in the process solution can be increased by increasing either the temperature, the NaOH concentration, or both [88–91]. As a result, operating conditions in plants vary widely. Higher digest temperatures result in higher pressures, making the equipment more expensive. There also is the need for more heat-exchange equipment, which further increases capital costs. High concentrations, on the other hand, permit in-

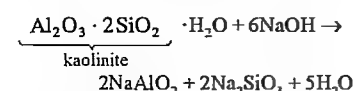
creased production from a given flow rate and, hence, from a given plant installation. Precipitation is thought to occur better at lower concentrations, but use of low precipitation concentrations while digesting at high concentrations requires dilution and additional operating costs for subsequent evaporation. Choosing digester conditions involves balancing these physical factors with local economics, together with the designer's experience. This has resulted in the spectrum of operating conditions given in Table 21.11.

Table 21.11: Commercial digestion conditions.

Bauxite type	Temperature, K	c_{NaOH} , g/L	Final $c_{\text{Al}_2\text{O}_3}$, g/L
gibbsitic	380	260	165
	415	105–145	90–130
boehmite	470	150–250	120–160
	510	105–145	90–130
diaspor ^a	535	150–250	100–150

^a CaO is added to digests to accelerate dissolution of diaspor.

The conditions listed in the first line of Table 21.11 are those for digesting bauxite at the atmospheric boiling point. Quite high alkali concentrations are required and the evaporation requirement is an extraordinary 5.3 t of water for a ton of Al_2O_3 . Most plants digesting gibbsitic bauxite use the conditions on the second line of Table 21.8. Boehmitic bauxite is digested using one of two general sets of conditions. The first is European practice, in which higher concentrations and dilution prior to precipitation are preferred to higher digest temperatures. When American companies began processing boehmitic bauxite from the Caribbean area, most chose the same concentrations used for gibbsitic bauxites; therefore, a higher temperature was required. The second important reaction in digestion is desilication. In the equation below, kaolinite is used to illustrate the reaction of siliceous minerals with the process solution:



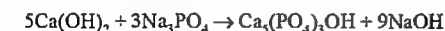
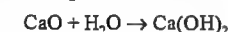
The soluble products react to form a series of precipitates with zeolite structure, having a

composition of approximately $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$.

Depending on temperature and concentration, the ratio of $\text{Al}_2\text{O}_3:\text{SiO}_2$ in the zeolite (tectosilicate) structure can vary. For each Al^{3+} replacing Si^{4+} in the lattice, one Na^+ is taken up to maintain charge neutrality. Anions, such as SO_4^{2-} or CO_3^{2-} may substitute for OH^- in the structure. The formation of the zeolitic desilication product (DSP) therefore leads to costly loss of sodium hydroxide. This reaction, however, is necessary for lowering the level of dissolved SiO_2 to less than 0.6 g/L, the maximum acceptable concentration.

The rate-determining step in the desilication reaction is the nucleation and crystallization of the desilication product. Therefore, the presence of seed particles is important; without seeds, solutions containing 0.75 g/L SiO_2 will not react in 40 min at 415 K. This has led to the paradoxical situation that some bauxites contain too little reactive SiO_2 for good desilication. The slurry blending and storage operation discussed earlier can be an important part of the desilication process. If the storage temperature is above 355 K, about 80% of the reaction takes place in 8 h. More important, seed is formed so the desilication reaction in the digester is not delayed. Very low SiO_2 concentrations can be achieved if an excess of CaO is charged. At high temperatures, and with the lime additions, a less soluble desilication compound (cancrinite) is formed. European plants use longer holding times during or after digestion to facilitate desilication.

Some CaO is added to the digest even when extreme desilication is not required. The calcium reacts with the carbonate and phosphate compounds as follows:



The last reaction controls the level of phosphates in the process solution; this impurity can affect clarification adversely. Causticization in the digest was more important when prices were such that the sodium required by the process was supplied more cheaply as

Na_2CO_3 . Its current importance is in control of the CO_3^{2-} concentration, which, at high levels, can affect precipitation. In modern practice, the causticization reaction is carried out on dilute process solutions outside the digester. Maintaining low concentrations and having much of the NaOH combined as NaAlO_2 are favorable to more complete reaction of CO_3^{2-} with Ca^{2+} .

Equipment

The equipment for digestion includes the reactor vessel, heat-exchange equipment, and pumps. The first reactors were horizontal vessels with crude agitators mounted on axial shafts. These were filled with a slurry of bauxite, lime, and process solution. They were closed and heated individually by injecting high-pressure steam. At the end of the designated holding time, a discharge valve was opened and the slurry was forced into another vessel at atmospheric pressure. Only a small portion of the steam flashing from the slurry as the pressure was reduced could be recovered. Continuous operation was introduced in the 1930s in which heat could be exchanged between the hot stream leaving the digester and the cooler, incoming stream. This greatly reduces the energy requirements.

Reactors. Digester vessels, whether batch or continuous, provide intimate contact between the bauxite and the solution for a period long enough to complete the extraction and desili-

cation processes. The equipment designed for this purpose is quite diverse. Agitated horizontal vessels have been replaced by vertical units to avoid the mechanical problems with sealing the agitator shaft. Both designs have used a series of vessels to minimize short-circuiting of the flow. European practice includes use of a series of vertical agitated vessels, each operating at a higher temperature than the preceding one. These units are heated by flashed steam in internal steam coils. A German digester design uses concentric pipes; the liquid being heated flows through the inner pipe while the hot slurry from the digester is returned through the outer pipe. This tube digester has been modified by placing several tubes for the cold slurry in parallel inside a larger outer tube. This reduces the length of the unit. The variety of digester design is illustrated in Figures 21.23 and 21.24. The flow through single-digester units may be as high as $12 \text{ m}^3/\text{min}$.

The usual *construction material* for digesters is mild (low-carbon) steel, despite data showing that, at the temperatures and NaOH concentrations involved, there may be stress corrosion cracking resulting from alkali embrittlement. The presence of the $\text{Al}(\text{OH})_4^-$ ions reduces the activity of OH^- in the solution. Finely divided Fe_2O_3 in the bauxite quickly saturates the solution with Fe^{3+} , suppressing corrosion of the metal. Some digestion equipment has been nickel plated for safety.

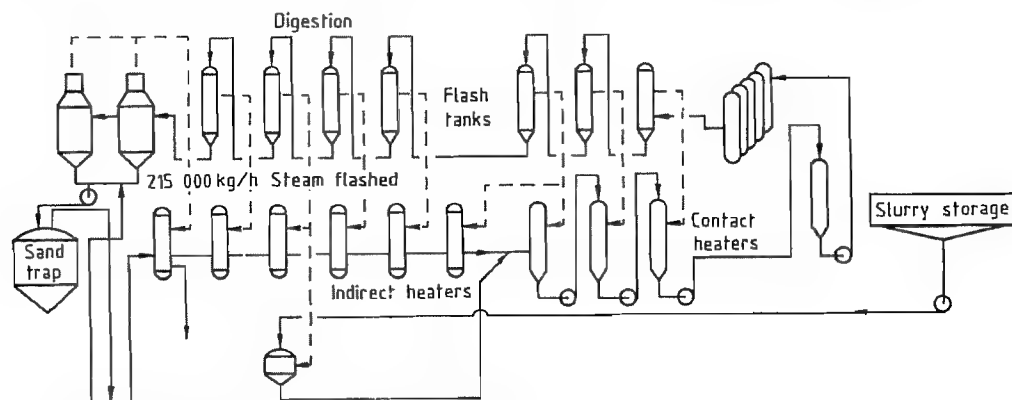


Figure 21.23: High-temperature digestion and heat recovery.

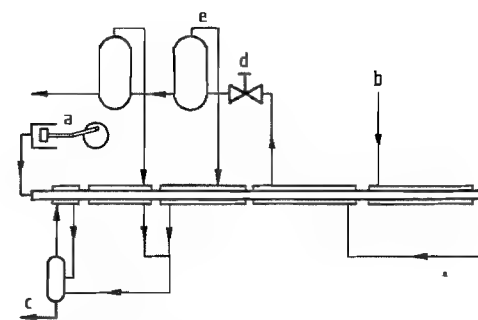


Figure 21.24: Tube digester: a) Piston pump; b) Heat; c) Condensate; d) Flow control valve; e) Steam.

Flashing. In most plants the hot slurry from the digester is flashed in a series of pressure vessels until it reaches the atmospheric boiling point. The steam generated in flashing is used in heat exchangers to heat the flow of liquor and bauxite coming to the digester. Flashing also removes water from the process stream, thereby accomplishing a significant portion of the evaporation needed. Normally, heaters are tubular, but coils of tubing also are used. As few as three stages of flashing may be needed when the digestion temperature is 418 K, and this may be increased to ten stages for a unit operated at 515 K. Figure 21.23 is a schematic diagram of a high-temperature digestion unit.

Heat Exchangers. Operating practice has been divided as to whether the bauxite slurry should be heated separately or whether it should be mixed with the rest of the solution and then heated. These two modes of operation have been designated the single- and the double-stream processes. Those favoring separate heating of the bauxite slurry, the double-stream option, feared rapid deposition of desilication product on the heat-transfer surfaces. Experience has shown that, particularly if the bauxite slurry is stored for blending, those fears are unfounded. The rate of fouling is no higher than for heating clean liquor. In both options there is slow deposition of desilication product on the heat-exchanger surface because the desilication reaction does not reach equilibrium in the digester and continues at a slow rate wherever the solution temperature is raised. The encrustation must be

removed periodically by washing with dilute HCl or H_2SO_4 , or by mechanical means to maintain a high heat-transfer rate.

In some plants using the double-stream system, the bauxite slurry is heated in contact heaters. These heaters are designed much like barometric condensers. The liquid is forced to fall through the steam in the heater in droplets or in thin films. The large surface area exposed results in high heat-transfer rates, and because there is no metallic surface, there is no fouling. The penalty is higher dilution.

The heat needed to raise the temperature above that achieved in the flashing system can be introduced by direct injection of steam. More often the final heating to the digest temperature is done in a separate heat exchanger, with the energy coming from steam, hot oil, or molten salts.

Pumps. *Centrifugal pumps* are used in most digester systems. Those used for pumping slurries are built of wear-resisting alloys. A great deal of maintenance is required to keep the shaft seals operating well. In some plants, concern about pump wear has led to the use of *diaphragm pumps*. In such pumps a check valve admits the slurry to a chamber on one side of a flexible diaphragm. When that chamber is full, oil at high pressure is forced into a chamber on the other side of the diaphragm. This moves the slurry through another check valve into the digester. Therefore, no rapidly moving parts are in contact with the slurry. In a Japanese modification, called the *Hydrohoist*, the diaphragm is replaced by a sphere that is free to move the length of a cylinder. Slurry is kept in one end of the cylinder and the drive fluid, which is clean process solution, is in the other end. Because of this choice of drive fluid, leakage past the sphere is of no consequence and tight clearances are not required.

Measurement and Control. Operating variables that must be controlled are temperature, solution concentration, and degree of desilication. The holding time is fixed by the design of the digester vessels. As noncondensable gases are formed by the reaction of the solution with

organic materials in the digest, it is necessary to vent these gases so that the digester remains full. Venting can be controlled by sensing the liquid level with a float or a radioactive sensor. Temperature measurement and control are relatively simple because only the temperature from the final heater is critical. Concentration control comes from blending the bauxite and careful proportioning of the slurry and clean solution flows. Originally, feedforward control was used in which the composition of the incoming materials was used to set the rates at which they were added. In modern practice feedback control is based on the composition of the exiting solution. Chemical analyses of the solution can be used, but the time lag involved makes this control imprecise. Nearly real-time control has been achieved by using the fact that the conductivity of the solution at a given temperature is a linear function of the mass ratio of Al_2O_3 and NaOH . This is the variable of interest. In modern plants the output of the sensor goes to a computer, which in turn controls the amount of bauxite slurry pumped. Such control has reduced the variance in concentrations to about a third of the values experienced earlier. This permits operation closer to the maximum safe concentration with less risk of premature precipitation of Al_2O_3 in clarification.

Clarification

The next step in the process is the separation of bauxite residue solids from the solution. There is a wide variety of equipment and procedures used in this operation. The methods chosen depend on the quantity and properties of the residue.

The particle size distribution of the residue solids is usually bimodal. The coarse fraction over 100 μm in diameter is termed *sand*, whereas the rest of the solids are finer than 10 μm . The sand fraction may range from 5 to nearly 50% of the total. The lowest amounts are in the residue from Western Australian bauxite. In the plant the sand fraction is separated from the process stream in liquid-solids

cyclones or in more primitive settling devices. A variety of equipment, including Dorr, Hardinge, and Aikens classifiers, have been used to wash the sand free of process solution before it is discarded. In all of these units the sand moves countercurrently to the wash water so that a maximum of washing is done with a minimum of water. The wash solution is added to the balance of the process flow and proceeds to further clarification steps for removal of the fine solids.

In most plants the fine residue fraction is settled in raking thickeners of the type illustrated in Figure 21.25. These vessels may exceed 49 m in diameter. Some older plants used multideck thickeners. Difficulties in keeping the multideck units in balanced operation have led to almost exclusive use of single-deck units in new construction.

The desanded slurry is fed at the center of the thickener and clarified solution overflows at the perimeter. As the solution flows radially across the thickener both the horizontal and vertical velocities become very low. The solids, having a higher specific gravity than the solution, sink to the bottom of the thickener. A settling rate of 1.5 m/h is sufficient for commercial operation. The solution overflowing the thickener usually contains less than 0.3 g/L solids, whereas the underflow ranges from 15 to 35% solids. The rotating mechanism has plows mounted at an angle to the arm. These slowly move the settled pulp across the bottom of the thickener to a discharge port. A few units have been designed with the discharge at the perimeter rather than at the center.

The objective was to avoid the need to elevate the units to provide access to a center discharge.

The fine solids behave as a relatively stable colloidal suspension, so they settle slowly if not treated further. The addition of *flocculants* improves the clarity of the thickener overflow, the settling rate of the solids, and the solids content of the underflow pulp. Flocculants act by binding the very fine particles into flocs that may be several millimeters in diameter. The ratio of mass to drag forces is increased so the flocs settle more rapidly.

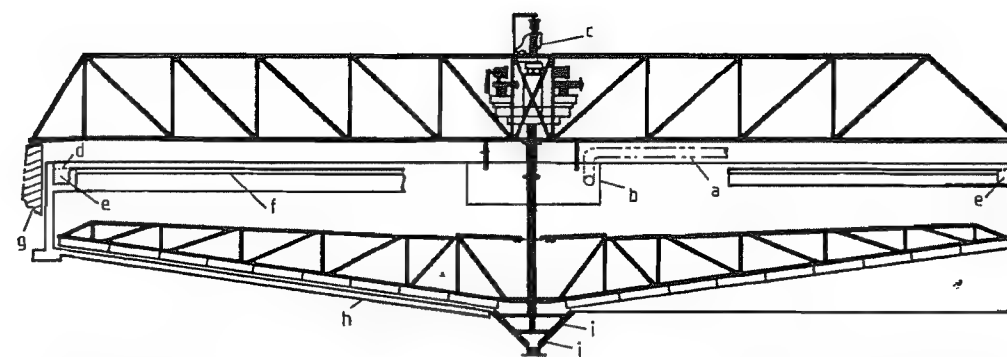


Figure 21.25: Residue thickener: a) Feedpipe; b) Feedwell; c) Motorized lifting device; d) Liquid level; e) Overflow launder; f) Weir; g) Off-tank support; h) Tank; i) Cone scraper; j) Discharge cone.

Starch from either grains or roots was the first flocculant; the dosage varied from 0.5 to 3 kg per ton of bauxite. The amount required increases as the surface of the residue increases and is affected by the mineral composition of the residue. Starch has the advantages of being inexpensive and ubiquitous. It does react with the NaOH in the solution to add organic compounds to the solution. In the 1950s water-dispersible polymers were proposed as flocculants. The first compounds were effective when added at 10% of the starch charge, but they were expensive so they offered no economic advantage. More recently, flocculants based on acrylate-acrylamide copolymers have begun to replace starch. The functional groups of these anionic flocculants can be modified to suit specific operating conditions. Different materials may be used in the thickeners and in the washing operation. In some cases a small amount of starch is added to the synthetic flocculant to improve overflow clarity. These synthetic materials now offer an economic advantage because they have been made less expensive and more effective.

With the residue concentrated in the thickener underflow, the next task is to wash it free of process solution so that it can be discarded. This is usually done in countercurrent decantation systems using washing thickeners that are similar in design to those used for settling. The washing operation is done in as many as seven stages with the solids moving countercurrent to the wash stream. This is illustrated

in Figure 21.26. An equation can be written for each stage expressing a material balance between soluble materials and dilution. Computer models of the washing system allow accurate prediction of performance.

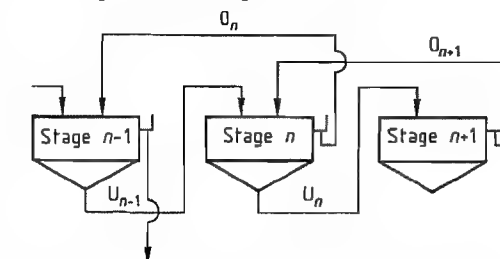


Figure 21.26: Flows at stage n in countercurrent decantation (O = overflow; U = underflow).

In *residue washing*, the objective is to minimize both the value of the soluble salts lost and the cost of evaporating the added wash water. The solubles in the discarded pulp can be reduced by increasing the solids content of the underflow. This reduces the amount of solubles carried from one stage to the next so that dilution is more effective and can be accomplished by using more flocculant or by increasing the holding time in the thickener. There is some risk in the latter change. If some undissolved gibbsite or boehmite remains in the residue, it may induce precipitation with a resulting loss of Al_2O_3 .

In some plants vacuum drum-type washing filters are used to replace some or all of the washing thickener stages. The solids content of the residue may be increased to 50–60% by

filtration. Therefore only about 33% as much solution is needed compared to plants using thickeners and this results in a great increase in the effectiveness of washing. Calculations for countercurrent washing show that two stages discharging at 55% solids are more effective than six stages operating at 20% solids.

Another approach only recently introduced into plant practice is called the deep thickener. This equipment was developed in the British coal industry to concentrate the slimes from coal washing. In the deep thickener, increased quantities of flocculant are used and a column of residue pulp up to 10 m deep is maintained. The hydraulic pressure of the deep column appears to densify the pulp so that underflow solids approaching the concentration of filter cake are obtained. The overflow from these units contains more solids than the flow from standard thickeners, but the units are finding use in concentrating residue for washing and for disposal. The simplicity of the equipment adds to its appeal.

The final stage of clarification is *polish filtration* of the solution, sometimes called clear pressing. Most of the residue solids have been removed from the process solution in the previous steps, but product purity must be protected by removing the few particles of solids remaining. Filter presses are used most widely.

Another approach to polish filtration is use of a stationary filter in which the medium is uniform, fine sand a meter deep. Gravity provides the force to move the solution through the sand bed. During operation, the fine solids are mixed with the sand, from which they are elutriated at the end of the cycle. Such filters can be automated and are especially effective with residues that are difficult to process.

Close attention is required to keep the solids content of the filtrate down to 0.5 mg/L to protect product purity. Light transmission of the filtrate is used as an index of clarity. Purity originally was determined visually, but nephelometers are used now. If evidence of solids is found, the filtrate from each filter is scanned to locate the source. Some solids may

pass through the filter cloth before a layer of solids forms to serve as a barrier, so it is common practice to recycle the first portion of filtrate.

Control in clarification has two major objectives; the solids must be removed and the washed residue must be prepared for discard, using a minimum of wash water. The first objective is achieved by measuring the cloudiness of the filtrate. High solids in the underflow are dependent in part on the retention time in the thickener, so measurements must be made of the pulp level in the unit. Automatic determination of the interface between clarified liquid and pulp has been done by ultrasonic and by optical scanning. The density of the underflow pulp is monitored by a device measuring absorption of radiation or by gravimetric measurement. If the pulp is too dilute the rate of withdrawal is decreased. This control can be overridden if the pulp level in the unit rises too high so that there is concern that the solids in the filter feed may become excessive. The flows of solids and wash water also must be measured and proportioned for efficient operation.

Precipitation

The filtered solution is at a temperature of 375 K and it must be cooled to 335–345 K before precipitation. This *cooling* is usually done in a flashing system analogous to that used in recovering heat in digestion. Because the temperatures are below the atmospheric boiling point, the flash vessels and the heat exchangers must operate under vacuum. This requires a method for removing noncondensable gases from the system. Usually a steam jet pump is used. Most heat removed by flashing is transferred to the colder solution returning from precipitation. Heat from the final cooling stage is ejected to the atmosphere or, preferably, to wash water entering the plant. Barometric condensers can be used for this final cooling. A recent development is to cool the solution further midway through the precipitation operation. This allows higher recovery of

Al_2O_3 without using conditions that lead to excessive nucleation of product.

Recovery of the $\text{Al}(\text{OH})_3$ from the process solution is known as precipitation, decomposition, or Ausrührung. The reaction is the reverse of the digester reaction given earlier. The cooling done after digestion and filtration has moved the solution into an area of the solubility diagram known as the metastable region. The concentration and temperature are such that the solution is supersaturated with $\text{Al}(\text{OH})_3$ but is not saturated enough for spontaneous crystallization. This is illustrated by Figure 21.27. At the digest temperature, T_1 , the Al_2O_3 concentration is increased to point P on the diagram. Cooling to temperature T_2 results in crossing the solubility curve into the metastable region. Addition of $\text{Al}(\text{OH})_3$ seed at this point causes precipitation and the concentration of Al_2O_3 approaches the solubility curve at T_2 . The additional cooling recently adopted moves the solution conditions further to the left in the diagram above a lower point on the solubility curve.

The kinetics of the precipitation reaction are represented by the equation:

$$-\frac{dc}{dt} = ke^{\frac{-E}{RT}}A(c_i - c_\infty)^2$$

where: $c = \text{Al}_2\text{O}_3$ concentration in g/L, $k = \text{constant}$, $E = \text{activation energy, about } 59\,000 \text{ J/mol}$, $R = 8.31441 \text{ J/mol}^\circ\text{K}^{-1}$, $T = \text{temperature in K}$, $A = \text{seed area in m}^2/\text{L}$, $c_\infty = \text{concentration at equilibrium}$.

The reaction is second order, i.e., the rate is affected by the square of the difference between the actual Al_2O_3 concentration and the equilibrium concentration. The operating temperature affects the equilibrium concentration and the reaction rate. Because seed area is important, the seed charge must be as high as can be maintained while meeting other operating objectives.

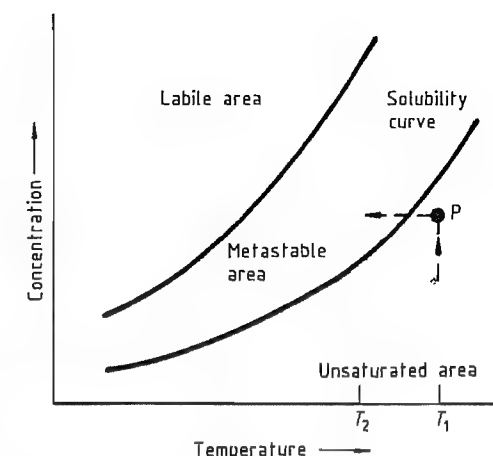


Figure 21.27: Generalized solubility curve.

The first objective in precipitation is to produce $\text{Al}(\text{OH})_3$ that, when calcined, meets the specifications for metallurgical alumina. These specifications are discussed in Section 21.10.1.5. The second objective is to obtain a high yield from each volume of solution. This increases the plant capacity and reduces the amount of energy spent in heating and pumping the solution. At the same time, the processes serving to create new $\text{Al}(\text{OH})_3$ particles must be controlled so that the number of seed particles created equals the number of particles leaving the system as product. This requires balancing nucleation, agglomeration, growth, and particle breakage, so a combination of science and art has developed.

About 2×10^{10} nuclei must be formed in each liter of solution to balance the process. The rate of *nucleation* is a strong function of both the degree of supersaturation and of temperature. Very few nuclei are formed if the temperature is above 350 K. A change in the operating temperature of only five degrees will change a system from a net producer to a net consumer of nuclei. Temperature changes of two to three degrees are the most frequently used control measures.

The nuclei *grow* slowly by accumulation of $\text{Al}(\text{OH})_3$ on their surface if they become large enough to be viable seeds. The rate of growth can be as high as 9 $\mu\text{m/h}$, but it is generally much lower. The growth rate is independent of

the particle diameter. Particles also increase in size by *agglomeration*. By a process that is not well understood, the nuclei form clusters in the first few hours of the cycle in batch precipitation. When the supersaturation is low, this agglomeration does not occur. Some speculate that when the rate of precipitation is high, the $\text{Al}(\text{OH})_3$ is not well crystallized when it is first deposited on the seed. This later may serve as the bond for agglomeration. At low supersaturation the deposited material is better ordered. The action of mechanical equipment in precipitation can *break* fragments off crystals or break up agglomerates, creating secondary nuclei, but this is not a major factor in most plants.

Figure 21.28 is an electron micrograph of some $\text{Al}(\text{OH})_3$ produced in a plant operation. The particles are obviously the result of agglomeration. Those agglomerates having fewer particles can be shown by thin-section micrographs to have grown radially from an agglomerate of relatively few nuclei.



Figure 21.28: Technical aluminum hydroxide (gibbsite), 200 \times .

In Figure 21.29, the Al_2O_3 concentrations in experimental precipitations is shown as a function of time and temperature. The slopes of these curves indicate the rates at which precipitation is progressing. All curves show a high rate at the start and appear to be approaching a final value asymptotically. The final concentrations were well above the saturation level, but in these as in plant opera-

tion the rate became unusually low, so the process was terminated.

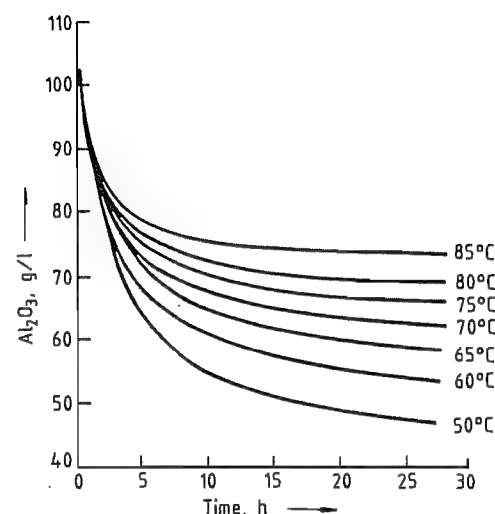


Figure 21.29: Effect of temperature on precipitation.

Precipitators are vertical cylinders; the height, which may be 30 m, is usually 2.5–3.0 times the diameter. The seeded slurry is circulated to maintain intimate contact between solids and solution. Early precipitators circulated the material by means of a central air lift pipe. Air introduced at the bottom of the pipe reduced the apparent density of the slurry within the pipe. This caused slurry to flow into the bottom of the pipe to establish circulation. Modern precipitators are circulated mechanically by impellers up to 3 m in diameter operating in a draft tube. In these units the flow is downward through the tube, so the tank bottoms are nearly flat to reverse the flow and cause upward motion of the slurry. Tanks with air lifts have conical bottoms to direct the flow to the central air lift.

Originally, precipitators were filled individually in *batch operation*. This method had several disadvantages, chief of which was the need for many operators because the operating cycle of a single precipitator required at least 15 separate operations. Control was difficult and batch operation left equipment out of service part of the time.

Nearly all plants built in the last 30 years have used the *continuous system*. Up to 13

tanks are placed in series so that the flow of seed and solution moves by gravity through channels connecting the tank tops. Continuous flows are much easier to measure and to automate. The number of flows is reduced, so control is better and the labor requirement is reduced. There are some operating problems. One is to avoid passage of the slurry across the tank tops, thereby reducing the retention time. Movement of solids from tank to tank is also a problem. An ideal system would retain fine particles in the tanks and move only the coarse material to the discharge. This is not possible, so a compromise method of operation must be found. Precipitation takes place at constant conditions in each tank instead of following a continuous curve, as in Figure 21.30. This tends to decrease production per tank, but the loss is more than recovered because the tanks are always in use.

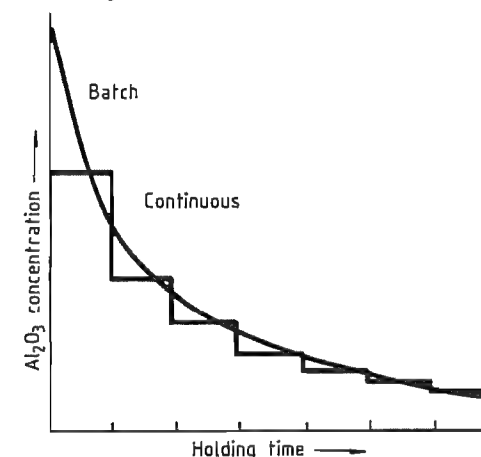


Figure 21.30: Al_2O_3 concentration profiles in batch and continuous precipitation.

Several patterns have been used to supply the *seed for precipitation*. The earliest was to neutralize a portion of the solution. An $\text{Al}(\text{OH})_3$ gel was precipitated that changed into fine crystallites on aging. This very fine material was grown through at least one cycle to provide an active seed for product precipitation. The more common approach is to use fine particles, produced in the operation, as seed. The slurry leaving precipitation is classified into a coarse product fraction and one or

more fine fractions. The fines are returned to the process to grow to product size. Classification is done by controlling the flow rate through tanks so that the fines are elutriated. Liquid solid cyclones are coming into use because they provide more accurate separations. The seeding and classification systems have become increasingly complex. In modern plants at least three fractions are separated. In some plants the agglomerates formed from fine seed must pass through the system once more before becoming product. This reflects the belief that the agglomerates must be made tougher by deposition of additional $\text{Al}(\text{OH})_3$ so that they do not disintegrate in calcination and subsequent handling.

In a recently disclosed modification [131], a relatively small charge of fine seed is added to the first tank in a series. This promotes agglomeration. Then, additional coarser seed is added to the second or third tank to provide the large seed area needed for high production. As indicated previously, cooling may be done between units in a series to increase the supersaturation in the final tanks, thereby increasing the production rate. A further change in modern plants is to filter the seed slurry being recycled. This decreases the amount of spent solution returning to the system and increases both the Al_2O_3 concentration in the first tank of the series and the overall production.

The control variables available to the precipitation operator are the temperatures in the system; the flow per unit, which translates into holding time; the amount of seed; and the particle size of the seed. Some of these variables are difficult to control, so the system usually cycles slowly from coarser than desired to finer. There is enough inventory in the process so that minor cycles can be tolerated without affecting plant output.

Impurities

The impurities in the product Al_2O_3 are affected by all of the foregoing operations, including selection of the bauxite. There are at least three classes of impurities. The first is residue solids that are not removed in clarifi-

cation. The large surface area of $\text{Al}(\text{OH})_3$ in precipitation effectively sweeps up these solids into the product. The preventive measure is increased vigilance in filter maintenance and operating. The second class is materials that are in true solution, such as sodium and gallium. The third group includes materials that are in solute form at the temperatures of digestion but precipitate later in the process. Their solubilities may be only milligrams per liter and return of the solution to equilibrium at lower temperatures may be slow. If precipitation is not completed before filtration, the remaining impurities appear in the product. There are also other impurities that do not fall neatly into these categories.

Sodium is the main component of the process solution and is also the largest contaminant of the product. The Na_2O content of alumina can be decreased by increasing the seed charge and by increasing the precipitation temperatures. The real variable that these operating changes help control is the rate of crystal growth. Higher temperatures, greater seed area, and lower Al_2O_3 concentrations all slow growth and give impurities more time to diffuse from the surface. By proper control of these variables an order of magnitude decrease in the Na_2O content of a commercial product has been achieved. Some sodium is lost in the Hall-Héroult cells during smelting by absorption into the cell lining and by conversion to sodium metal, so complete absence of sodium in metallurgical alumina is not necessary. The target is to balance the input to the cells with the losses. This requires Al_2O_3 containing about 0.4–0.5% Na_2O .

Gallium is a ubiquitous component of aluminous ores. Its chemistry is similar to that of aluminum, so it accumulates in Bayer process solutions until an equilibrium is reached at about 0.2 g/L. The gallium content of Al_2O_3 is a linear function of the gallium concentration in the solution. Therefore, the amount leaving in the product equals the input. Because gallium is in true solution, the same changes that lower the Na_2O content of the product lower the gallium content. Only in the production of high-purity metal has there been concern

about the gallium content of alumina. About 10 t/a of gallium is recovered from Bayer process solutions. This is the best source for the production of gallium.

Silicon is a component of many aluminum alloys, yet the specification for Al_2O_3 is less than 0.02% SiO_2 . This value is only 25% of that specified 50 years ago. The SiO_2 is in solution, but it appears to be added to the product through a slow continuation of the desilication reaction. There is also evidence that if the rate of Al_2O_3 deposition on seed is not high, the seed surface becomes at least partially covered with desilication product, thereby becoming less active as a seed for $\text{Al}(\text{OH})_3$ precipitation and more active toward SiO_2 . This impurity is controlled by driving the desilication reaction nearer to completion. Lowering the SiO_2 concentration of the solution below 0.1 g/L gives a product containing less than 0.003% SiO_2 .

Potassium is undesirable in the Al_2O_3 because it may destroy the graphite in Hall-Héroult cells by intercalation, i.e., it diffuses between the layers of the graphite structure, thus expanding its volume. Although it is soluble in Bayer solutions, there has not been a recorded instance of K_2O concentrations becoming high enough to affect the Al_2O_3 quality.

Iron(III) oxide (Fe_2O_3) as an impurity in Al_2O_3 has been the subject of much investigation. It is soluble up to ≈ 1 g/L in the solutions at digest temperatures (400–500 K), but only to ≈ 0.001 g/L at 333 K [132]. This reconciles the observations that Fe_2O_3 behaved at times as if it were in solution and as a colloid at others. There are several iron minerals that can serve as sources for the impurity. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeO}(\text{OH})$) are present in most bauxites. Goethite is slowly converted to hematite in high-temperature digests, particularly if CaO is present. This conversion improves clarification because hematite settles better than goethite. The mineral siderite (FeCO_3) present in some bauxites not only is a source of iron but also reacts with NaOH to increase the amount of causticization needed. Pyrite (FeS_2) is almost insoluble in Bayer so-

lutions; its adverse effects occur when the sulfur is oxidized to sulfate in the presence of air and water. The sulfate will react with NaOH to form Na_2SO_4 which has to be removed periodically.

Paradoxically, there is less difficulty with Fe_2O_3 as an impurity in processing bauxites containing a large amount of iron oxides. This is probably because the iron oxides serve as seed and hasten hydrolysis of the NaFeO_2 formed in the digest. Running the solution over iron oxide particles before filtration has been effective in controlling this impurity. Another process for lowering the iron content of Al_2O_3 is termed step precipitation. The filtered Bayer solution is lightly seeded with $\text{Al}(\text{OH})_3$ for a short time to precipitate up to 3 g/L Al_2O_3 . The seed and the small amount of precipitation effectively sweep the colloidal iron hydroxide particles from the solution, leaving an Fe_2O_3 concentration of less than 0.005 g/L.

Calcium also is a common impurity. The presence of increasing amounts of Na_2CO_3 in the Bayer solution seems to increase the CaO in the product. The CaO is not harmful to the aluminum produced; there is calcium in the Hall-Héroult cell bath. As with sodium, additions to the cells should not exceed the losses to avoid buildup in the electrolyte. Calcium can be controlled by step precipitation or by lowering the carbonate content of the solution. Another alkaline metal, *lithium*, also is acceptable in Hall-Héroult cells. It can be removed by step precipitation.

The *other metallic impurities* that appear in many bauxites in small amounts are chromium, copper, manganese, titanium, vanadium, and zinc. Generally, these impurities are not so concentrated that removal processes are required. Sulfide salts have been added to precipitate copper and zinc. The chromium is a problem only if it is oxidized; the organic salts in the solution are usually a sufficient reductant. The addition of manganese compounds as oxidants for organic material has been reported.

Anions, such as carbonate, chloride, fluoride, and sulfate, are known to interfere with $\text{Al}(\text{OH})_3$ precipitation. The carbonate ion is

controlled by addition of lime, although processes have been reported in which Na_2CO_3 is removed by evaporative crystallization or by cooling the solution to 260 K. The sulfate and chloride ions usually are controlled naturally, as their salts are incorporated in the desilication product in sufficient quantities to maintain an equilibrium. There are commercial operations in which the sulfate salt is removed by evaporation and crystallization. The least soluble salt is schairerite ($\text{Na}_2\text{SO}_4 \cdot \text{NaF}$), and when the fluoride ion is depleted, burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) appears. The fluoride ion is almost never present in quantities large enough to be harmful.

Many bauxites contain *phosphate minerals*. Apatite ($3\text{Ca}_2\text{P}_2\text{O}_8 \cdot \text{CaF}_2$) does not react in the process; indeed, this compound or its hydroxy counterpart is formed when soluble phosphates react with calcium in the digest. Aluminum phosphates, such as wavellite ($4\text{AlPO}_4 \cdot \text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$) do react, forming Na_3PO_4 as the soluble phosphate. The phosphate ion interferes with flocculation of bauxite residues containing goethite, probably by competing for attachment sites [133]. The concentration of phosphates never is high enough to interfere with Al_2O_3 purity. Addition of CaO to the digest is the control measure.

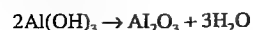
The *organic matter* in bauxite, whether it be roots and twigs from plants or humic acids from decayed matter, reacts in the digest to form a wide variety of organic compounds. Some operation process streams have exceeded 15 g/L organic carbon in solution. There is evidence that larger molecules are oxidized in the process all the way to Na_2CO_3 and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$). In addition some, but not all, of the organic compounds may interfere with precipitation [91].

The effect of sodium oxalate on processing has not been quantitatively determined, yet many plants incorporate equipment for crystallization of the oxalate salt from the solution. Others wash this salt from the $\text{Al}(\text{OH})_3$ seed and recover it from the wash water. The evidence is overwhelming that operations are improved by the oxalate removal techniques. Early removal processes included evapora-

tion to high concentrations followed by centrifugal separation of the gelatinous salt mass. In other plants, a portion of the solution was mixed with bauxite or $\text{Al}(\text{OH})_3$ and heated to 1280 K. This destroyed the organic compounds and formed NaAlO_2 , which could be recovered in the process. A German process adds magnesium salts to the digest to remove the deleterious organic compounds. Still others are investigating methods of oxidizing the organic material in the solution [134].

Calcination

The final operation in production of alumina is calcination. The temperature of the $\text{Al}(\text{OH})_3$ is raised above 1380 K resulting in the reaction:



As discussed in Section 21.10.1.2, this reaction can take several pathways and several transition forms may appear. The end of all pathways is α -alumina. In older European practice, a major portion of the alumina was converted to the α -phase, sometimes by the addition of a fluoride salt to lower the temperature of transformation. In American practice,

calcination always has been less severe; so, normally, $\leq 20\%$ of the alumina is in the α -phase.

Before calcination, it is necessary to wash the process solution from the coarse $\text{Al}(\text{OH})_3$. This is done countercurrently, using storage tanks and filters. As in residue washing, increasing the number of washing stages and the concentration of solids leaving each stage improves the effectiveness of washing. Vacuum filters of several designs have been used for the final separation. The early Oliver and Dorr drum filters have been replaced by horizontal rotary filters because better washing can be achieved. The quality of the wash water is of some concern because such impurities as calcium and magnesium can be adsorbed on the surface of the $\text{Al}(\text{OH})_3$.

Previously, calcination was done in reverberatory furnaces. These had neither the capacity nor the thermal efficiency required, so they were soon replaced by *rotary kilns*. These kilns are cylinders that may be 3.5 m in diameter and over 80 m long. They are mounted on bearings and rotate about an axis inclined at a small angle to the horizontal.

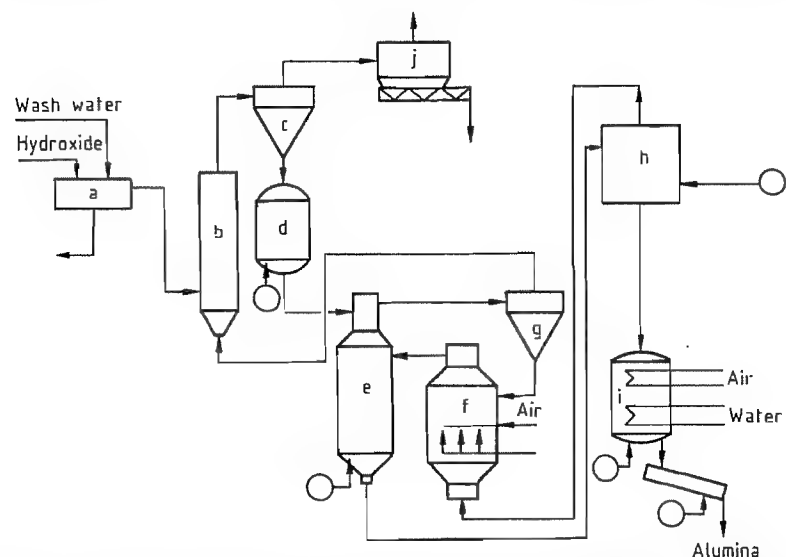


Figure 21.31: Alcoa flash calciner: a) Filter; b) Flash dryer; c) Cyclone; d) Fluidized-bed dryer; e) Holding vessel; f) Furnace; g) Cyclone; h) Multistage cyclone cooler; i) Fluidized-bed cooler; j) Electrostatic precipitator.

Damp $\text{Al}(\text{OH})_3$ from the filters enters the upper end and slowly tumbles toward the lower end, traveling against a stream of hot gas formed by combustion of natural gas or oil at the discharge end. Early kilns were less than 40 m long, but longer units have better thermal efficiency and higher capacity.

Product coolers were added to kilns so that part of the heat in the incandescent product could be transferred to the combustion air. Early coolers followed designs developed in the cement industry and were themselves rotary units much like, although smaller than, the kilns. Improved coolers fluidize the product Al_2O_3 around heat-exchange surfaces, often in several stages. In such coolers, the heat can be recovered in combustion air or in wash water and the product can be cooled readily to 425 K. The best rotary kilns require about 4800 MJ per ton of product.

Rotary kilns are being replaced by *stationary calciners*. In stationary calciners, a combination of fluid beds and stages in which the solids are transported in suspension is used. Figure 21.31 is a schematic diagram of a commercial unit capable of calcining 1500 t/d.

The $\text{Al}(\text{OH})_3$ is washed and dewatered on the filter (a) and is conveyed into the flash dryer (b), where it encounters hot gas from cyclone (g). The gas evaporates the free water from the particle surfaces. Because the temperature exceeds 480 K, a portion of the water of hydration also is driven from the crystals. Cyclone (c) separates the solids from the gas. The gas, cooled almost to its dew point, leaves the unit through the electrostatic precipitator (j), where dust is recovered. Vessel (d) serves as a surge buffer to smooth the flow of solids through the unit. The solids are separated in cyclone (g) to enter the vessel (f) where combustion of fuel is taking place. Vessel (e) allows a holding time at the calcination temperature so that the water content of the product is low. A small amount of fuel can be burned in this vessel if a higher temperature is desired. In this design the flow of solids is counter to the flow of the gas.

The solids are cooled, also in counterflow, by the combustion air in unit (h). Final cooling

is in a fluidized-bed unit (i). In the fluidized unit a small amount of air is introduced through a membrane at the bottom. This lifts but does not entrain the solids, so they behave much like a fluid. Heat is transferred at high rate to air or water flowing through tubes submerged in the bed. The product Al_2O_3 can be cooled below 400 K with all of the recovered energy being used in the process.

The great advantage of the stationary units is that the heat required for calcination is 3250 MJ/t. The capital costs are lower than for rotary kilns of equal capacity and the maintenance costs are lower primarily because the refractories are not subjected to rotational stresses. Because the capacity per unit is high and automation is quite easy, the labor requirements are low. The stationary units are being installed in retrofitting older plants as well as in new construction.

Alumina calcined in stationary kilns has a lower α -alumina content and a higher surface area than alumina calcined at the same temperature in a rotary kiln. This reflects the shorter residence time and the absence of a high-temperature flame in the static units. Photomicrographs show that the rapid temperature rise creates vapor pressure within the particles that tends to fracture large crystals.

The characteristics of the metallurgical alumina are controlled mostly by the time and temperature of calcination. The important control is the relation between the $\text{Al}(\text{OH})_3$ feed and the flow of fuel. The fuel must be free of impurities that can contaminate the alumina. Sulfur and vanadium in fuel oil are limited by concern for product purity. The amount of combustion air must be sufficient to burn the fuel completely without the use of a great excess that increases the gas flow and thereby reduces the thermal efficiency.

Evaporation

As is shown on the flow sheet for the Bayer process (Figure 21.21), the solution continuously cycles through the plant. Consequently, any wash water used must be evaporated so that the solution volume can be controlled.

About 10% of the flow is evaporated in the two cooling areas by being flashed into steam. In high-temperature digesters, the amount of flash evaporation is even larger. At least one plant processing high-grade bauxite was designed without any additional evaporation capacity. In most cases, the economics require installation and operation of evaporators. The objective is to minimize the summed costs of evaporation and the value of the soluble salts lost by incomplete washing. The minimum is usually attained with a net dilution of the residue of 1.5–2.0 kg/kg.

Table 21.12 lists the input and exit streams that compromise the dilution balance in an operating plant. Efficiency demands that all of these flows be monitored.

Table 21.12: Dilution balance.

Inputs	Losses
residue wash	evaporation
sand wash	—
Al(OH) ₃ wash	heat interchange flash
free moisture in bauxite	Al(OH) ₃ to calcination
water in gibbsite and boehmite	free water with Al(OH) ₃
injected steam	water with residue
purge water	vapor from solution surfaces
sodium hydroxide	
cleanup water (maintenance)	
uncontrolled dilutions	

Several evaporator designs are used in Bayer plants, but nearly all designs are used in *multiple-effect configurations*. In such units each stage operates at a lower pressure than the preceding one. Therefore, the vapor evaporated from the solution in the first stage is at a temperature high enough to heat the solution in the second stage, causing it to boil. This continues to the final stage, where the vapor is condensed. The condenser operates under vacuum so a jet pump is necessary to remove non-condensable gases from it. The more times the latent heat is used, i.e., the more stages that are present, the more water can be evaporated by the fuel steam used in the first effect. With Bayer solutions the maximum number of effects is six. This is because the boiling point of the solution is elevated 5–8 K by the dissolved solids. This reduces the steam temperature in each effect; with many effects there is little

temperature difference available to cause evaporation.

An unconventional design called *continuous regenerative evaporators* has been used in some plants. These units are similar to the heating and flashing equipment used in digestion in that the feed is heated through up to ten stages without evaporation; the hot solution is then flashed through an equal number of stages and the steam is used for heating the feed. These units are not as efficient as most multiple-effect evaporators. The design choice is based on economics. Special evaporator designs may be used when it is necessary to crystallize organic or inorganic salts from the solution. In such designs pumps are used to increase the thermally induced flow through the tubes in the heaters. The heat-transfer surfaces in evaporators must be cleaned periodically to remove encrustations of desilication product and soluble salts.

Evaporators are controlled primarily by changing the amount of steam used. The flow of feed solution is regulated so that crystallization of soluble salts is either induced or avoided, depending on the operating mode. Temperature readings at each effect are compared to design values to indicate operating difficulties.

Residue Disposal

The most important environmental problem in the Bayer process is disposal of the bauxite residue. The solution left with the residue after an economical amount of washing is still very alkaline and cannot be allowed to contaminate ground water. Furthermore, the desilication product in the residue which is in contact with water has the capacity to exchange sodium for hydrogen. An aqueous slurry of the residue that had been washed with 1000 times its mass of distilled water still reached a pH value of 10.5 on standing. The undrained fine residue, even after years of consolidation, does not have enough strength to support buildings or equipment. These properties make disposal a difficult problem.

Previously, disposal was to a marine environment where the alkalinity was diluted by large quantities of water. This method has been used in the seas off Europe and Japan and in a river in the United States. Studies by environmentalists have indicated little damage to flora or fauna by the residue in a disposal area [135]. Today, however, environmental concern is so great that any new refinery is unlikely to be permitted to use marine disposal.

Early inland refineries simply dammed a convenient valley or built retaining dikes on flat land to form residue disposal areas. In some cases, the sandy portion of the residue was used to build the dikes. This method can be effective and cheap if care is taken to protect the surroundings by proper sealing techniques. The compacted residue has a lower permeability than many clays; yet, there have been isolated leaks into aquifers from such impoundments. Improved designs have been developed.

In Germany, retaining dikes are built with a portion of the structure designed to be porous. The dilute solution draining from the residue is channeled by the porous sections into water-treatment facilities before being discarded. In some cases, the dike material exchanged ions with the solution so that little treatment was needed. The draining allowed consolidation of the residue so that it could support equipment. An American firm used a drained lake in which the bottom of the disposal area was covered with sand in which draining pipes were laid. The residue was pumped to these areas in the traditional manner as a dilute slurry. Most of the conveying water was decanted, while some percolated through the deposit to the drains. This design has two advantages: the residue consolidates better, so the storage capacity of an area is increased, and the hydraulic head on the bottom is reduced to zero, so that leakage is unlikely. Recent lakes have been built using the sand drains on top of seals of clay and plastic film for additional environmental safety.

Another modern disposal method, called *dry stacking*, takes advantage of the thixotropic nature of the residue. By some method,

usually vacuum filtration, the residue is concentrated to 35–50% solids. The slurry is agitated to reduce its viscosity by as much as two orders of magnitude and pumped to a disposal area. There it flows in lava-like fashion over the surface, establishing a slope away from the discharge point. In the absence of shear, the viscosity of the slurry increases and flow stops. Water does not separate from the slurry and the slope causes rain to run off rapidly, so the surface usually is losing water to the atmosphere. The surface becomes deeply fissured, further assisting drying. In about 90 days the residue may dry to 75% solids, far drier than in any of the other disposal methods. In this state, it can support heavy earth-moving equipment and can be recovered or used for increasing the height of retaining dikes. This method maximizes the storage capacity of a given area and seems to pose the minimum threat to the environment. It does require construction of a permanent lake area for water storage and for cooling water. If any use is to be made of the residue, recovery is relatively easy.

In some countries there is a requirement that the area devoted to residue disposal be returned to productive use. Some Australian residue areas have been covered with the sandy fraction of the residue. By the addition of organic matter and fertilizer, the area has been returned to agriculture. At the University of Georgia, microorganisms given the proper nutrients grew in the residue and produced simple organic acids that neutralized the alkalinity of the residue. Draining was needed so that high concentrations of sodium were washed away, then the residue could support plant and simple animal life. The addition of gypsum hastened the neutralization process, probably by forming the neutral Na₂SO₄. Agricultural use of residue areas is therefore possible after some effort and expense. The bearing strength of dry-stacked residue is sufficient to support homes and light industrial buildings.

Many investigations have been directed toward finding a commercial use for bauxite residue. The high iron content of some residues suggested production of pig iron. The quality

of the iron was poor and the amount of slag formed exceeded the original amount of residue. Similarly, chemical processes have been developed for recovery of Al_2O_3 , Na_2O , and TiO_2 from residue. Although all are technically possible, none has been feasible economically. Small quantities of residue have been used in making Portland cement, and smaller quantities have been used as a mold wash, as an insulating material, and, after reaction with H_2SO_4 , as a water treatment. No chemical use is likely to consume a significant part of the residue [88, 92].

The residue is claylike and can be used in ceramic materials. The sodium causes formation of glasses at 1450 K, giving a vitreous bond. Bricks have been made commercially, but economic factors and other shortcomings of the brick have eliminated this use. Sintering the residue into aggregate for concrete may be economical where natural aggregate is not available.

In Texas, agronomists have shown that the residue can be used to neutralize acidic soil, replacing limestone. The cost of preparing the material for application and the logistics argue against extensive use. The conclusion is that large-scale use of bauxite residue is unlikely, so efforts should be directed toward reclamation of disposal areas.

Energy in the Process

Approximately 16 MJ are required to produce a kilogram of Al_2O_3 . The worldwide range is 7.4–32.6 MJ/kg [136]. Variations in the quality of bauxite, plant design, and the size of the plants are the reasons for the wide differences. Even with existing plants, large improvement in energy usage can be made. The Aluminum Association (USA) reports that the energy used per unit of alumina production in 1980 was 68% of the energy used in 1972 [137]. The energy used in mining is less than 5% of the total and is difficult to change. The energy for transporting bauxite is double that for mining it, because the average ton of bauxite used in the United States is transported 4700 km. The situation worldwide is

different because much of the bauxite is refined close to the mines.

Within the refinery, more than half of the energy is used for pumping and heating the solution and for evaporation. The previous discussion has shown that plant design can affect heat recovery and minimize energy use. Emphasis is being placed on increasing the amount of Al_2O_3 recovered from less than 50 g/L to over 65 g/L; some claim yields as high as 80 g/L. Because energy is more closely related to the flow of solution than to yield, the energy savings are large. The static calciners are nearly as efficient as they can be made because the temperatures of the gas and of the product leaving the units are very low. The change from rotary kilns has made up a large portion of the savings. There are still opportunities to improve operating practice and design to reduce energy consumption [138].

Economic Aspects

The largest cost elements in alumina production are raw materials, energy, and capital-related costs for the production equipment. Labor, operating supplies, and miscellaneous costs are much smaller than these three.

Bauxite is the most important raw material. Its cost includes those for mining, transport, levies, and taxes. In addition, the relative quality of the bauxite ore influences the expenditures for necessary reagents. Mining is relatively inexpensive because most deposits are covered with only a shallow overburden and can be mined with efficient equipment. Since the formation of the International Bauxite Association (IBA), levies and taxes have become a large part of the cost of bauxite. These costs have become relatively stable because most are related to the selling price of aluminum. The availability of bauxite from outside the IBA countries has allowed the effect of supply and demand to influence this cost. Where levies are not imposed, some system of taxation provides income to the producing nation. Transportation costs vary from very small to as much as half the delivered cost of the bauxite. Some bauxite travels less

than 5 km by truck or conveyor belt to the refinery. Other bauxite may travel more than halfway around the world. The characteristics of bauxite most important in influencing its value are the available alumina and the reactive silica contents. The latter quantity has a great effect on the amount of sodium hydroxide and lime required in processing. Bonuses are given for high available alumina values, and penalties are charged for excessive silica.

In the previous section, values were given showing the fourfold range in energy used to produce alumina. The most important variables are the plant design and the quality of the bauxite being processed. The most energy-efficient bauxites are gibbsitic, with very low residue content.

The capital costs also show wide variation. In 1980 U.S. dollars, new installations may cost from \$400 to \$800 per annual ton of capacity. The variables are design factors, location, capacity, and the properties of the bauxite to be processed. Much of the world capacity was constructed before construction costs were inflated and so has lower capital costs. The effect of capacity is also large, and plants producing 2×10^6 t/a have costs well below those of plants producing less than 10^5 t/a.

There is more capacity for producing metallurgical alumina than there is smelting capacity. Not all smelters have alumina capacity dedicated to them; they buy alumina on contract. Long-term contracts are common. In other instances, alumina is bought when needed at spot market prices. Since 1980, alumina has sold on the spot market for less than \$150/t to over \$280, reflecting a change in the relationship between supply and demand. Economics do not always control production because many corporations own refineries to supply their smelters. In other instances, national governments own a significant portion of a refinery and for political reasons may choose to operate in a noncompetitive situation. Costs per ton of alumina can, under unfavorable conditions, exceed \$200, although efficient plants may produce at roughly half this figure.

21.10.1.4 Other Processes for Alumina Production

Raw Materials

Many investigators have sought processes to replace the Bayer process using raw materials other than bauxite [89]. Clay, primarily kaolinite, has been most considered because it can contain up to 39% Al_2O_3 . Other materials, including anorthosite, nepheline, coal wastes, and fly ash, have been candidate raw materials. Yet, less than 2% of the world supply of alumina is not made by the Bayer process. This happens only where use of a domestic raw material and production of a desirable by-product change the economic picture. Alumina from ores other than bauxite normally costs 1.5–2.5 times that from the Bayer process.

Because aluminum is amphoteric, both acid and alkaline processes have been developed. Most of the processes in each class follow the same general flow sheets.

Alkaline Processes

Sodium compounds, such as Na_2CO_3 , react at 1280 K with the Al_2O_3 in aluminous ores to produce water-soluble NaAlO_2 . This compound can be leached from the sinter with water and the solution treated to remove impurities; the purified solution is neutralized with CO_2 to recover $\text{Al}(\text{OH})_3$. The last step regenerates the Na_2CO_3 for recycle. Difficulty arises because the aluminous ores contain SiO_2 , which also reacts in the sinter to form soluble Na_2SiO_3 . In processing, the desilication reaction discussed earlier takes place, so the net recovery of Al_2O_3 is small or zero. If 2 mol of CaO , usually as limestone, is charged for every mole of SiO_2 in the raw material, insoluble calcium silicate compounds are formed. Under proper leaching conditions the NaAlO_2 can be recovered from such sinters with only slight loss.

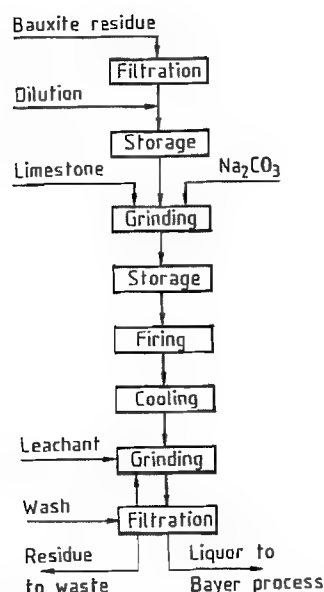
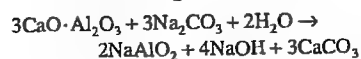


Figure 21.32: Lime/soda sinter process flow sheet.

This process has been used commercially in two American plants to recover most of the Na_2O and Al_2O_3 lost in the desilication product formed while treating high-silica native bauxite. A schematic flow sheet is given in Figure 21.32. The same process was investigated by the U.S. Bureau of Mines in a large pilot plant using anorthosite as the raw feed [139]. [Anorthosite is a mixture of the minerals anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and albite ($\text{NaAlSi}_3\text{O}_8$).] Unless the composition, sintering, and leaching were closely controlled, the residue formed a gel in leaching and became very difficult to filter.

In a variation of the sintering approach, *calcium* replaces the sodium so that calcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) is formed as well as calcium silicate (CaSiO_3). The calcium aluminate reacts with Na_2CO_3 in an aqueous leach to form NaAlO_2 .



In carbonation, $\text{Al}(\text{OH})_3$ is formed and the Na_2CO_3 solution is regenerated. Nepheline, $(\text{Na},\text{K})\text{AlSi}_3\text{O}_8$, is treated by this process in former USSR. The calcium silicate residue is processed to make about 10 t of cement per

ton of alumina. The two products make the process viable here.

In the Pedersen process, the sinter is replaced with a reducing fusion so that ferric ions in the ore were reduced to metal. Iron and the calcium slag were separated by decantation. During cooling, the CaSiO_3 passes through a crystalline phase change and the resulting stresses reduce the slag to powder [88, 89].

The sinter processes suffer economically for several reasons. The energy for sintering and for evaporation of the leach solution must be added to the energy required from operations analogous to those in Bayer processing. The capital investment is increased by the need for sintering equipment, and although limestone is inexpensive, the quantity required is so large that the expense is considerable.

Acid Processes

All of the acid processes follow the general flow sheet given in Figure 21.33. The clay is prepared by grinding and by roasting it to about 1000 K. The roasting changes the kaolinite to meta-kaolin, from which the aluminum can be dissolved as the acid salt. The roasted clay is leached in an acid solution, usually at the atmospheric boiling point. Some investigators have chosen to leach at elevated temperatures for processing advantages even though corrosion problems become more severe [88]. The siliceous residue is separated using sedimentation and filtration as in the Bayer process. Small amounts of iron salts remain in the clarified solution. These salts are removed by extraction with an organic compound that forms a complex with the iron but not with the aluminum salts. The organic solution is decanted from the aqueous phase and is treated to separate the iron salt and to regenerate the organic extractant.

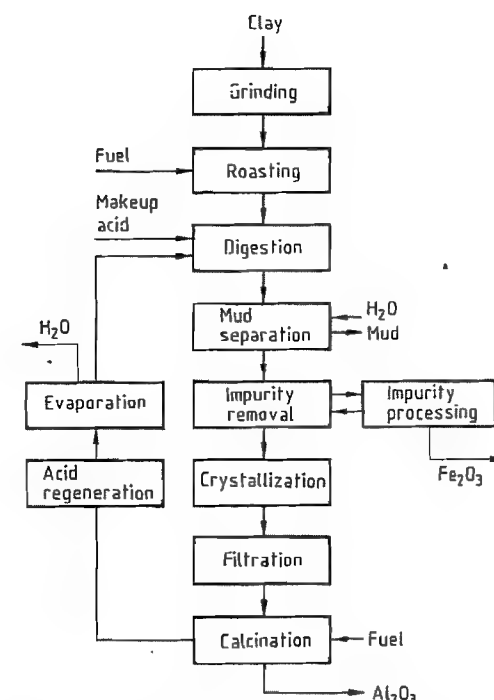


Figure 21.33: Generalized acid process flow sheet.

A hydrated aluminum salt is recovered from the aqueous solution, usually by evaporation and cooling to cause crystallization. In the *hydrogen chloride process*, advantage is taken of the low solubility of AlCl_3 in HCl . The HCl gas is absorbed in the solution both to regenerate the acid for leaching and to precipitate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. In all acid processes the hydrated salt is decomposed to Al_2O_3 by heating to 1300 K. Both water and the acid radical are driven off, and the acid is absorbed for recycling.

The U.S. Bureau of Mines sponsored a cooperative effort with several aluminum companies to investigate acid processes for recovery of alumina from clay [139]. For several reasons the HCl process was preferred: the reagent is inexpensive, processing conditions are not severe, the salt can be recovered without evaporation. The HCl is not decomposed in calcination, and the water content of the acid salt is half that of other acid salts. Despite these features the process is not competi-

tive economically with the Bayer process. A major fault is the amount of energy used to roast the clay, to evaporate the solution, and to decompose the acid salt. The investment is increased because of the corrosive solutions. A process disadvantage is that the Al_2O_3 is physically different from Bayer alumina, so smelting practice has to be changed for this aluminum source.

Pechiney and Alcan jointly operated a pilot plant using the H^+ process, a modification of the HCl process in which H_2SO_4 is added to the digest [140]. The combination of acids eliminated the need to roast the clay. Other processes use H_2SO_4 , H_2SO_3 , HNO_3 , or NH_4HSO_4 as reagents to attack the clay, but no commercial use has been made of any of them.

Clay is a major impurity of coal, so the ash from coal may be considered an overroasted clay. The acid processes, with minor modifications, will extract alumina from ash [140]. Anorthosite that is high in anorthite reacts with boiling HCl ; this approach has been investigated in Norway and Canada [141]. So far, all of these methods have served only to enrich the technical literature.

Two aluminous minerals that do not contain silica have attracted attention and, because of their composition, require different technology. Alunite, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ has been used commercially in Russia. Both H_2SO_4 and K_2SO_4 are useful by-products of alumina production by this method. The alunite is heated to drive off the hydrated water; additional heating under reducing conditions decomposes the aluminum sulfate without adversely affecting alumina recovery. The solid residue from the roast is a mixture of K_2SO_4 , Al_2O_3 , and gangue. The K_2SO_4 is dissolved in water and recovered. Alumina is extracted from the gangue in a modification of the Bayer process. In other approaches using alunite, the solutions are kept acidic so the alumina is recovered as a salt [142].

Dawsonite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CO}_2 \cdot 2\text{H}_2\text{O}$, is found in some oil shales. The temperatures used to recover the oil from the shale decompose the dawsonite to NaAlO_2 , which is soluble in dilute NaOH . The $\text{Al}(\text{OH})_3$ and Na_2CO_3

can be recovered from the solution by carbonation. The economics are such that recovery of the oil must be competitive before mining and by-product recovery can be considered.

21.10.1.5 Metallurgical Alumina

Aluminum production is the principal application for alumina; more than 92% of world alumina production is used for this purpose. The property requirements for commercial metallurgical alumina therefore are of considerable importance to the alumina industry. Specifications have responded to changes in energy costs, aluminum cell design, cell gas scrubbing techniques, environmental regulations, working conditions in smelters, and the technology for alumina calcination. In general, there has been a shift away from relatively small-particle-size, highly calcined, "floury" alumina to a coarse, free flowing, dust-free, less calcined, "sandy" alumina of narrower particle sizing and higher chemical purity.

Alumina Properties Required for Electrolysis

Five developments have had a significant impact on alumina properties.

Cell Design. New, high current efficiency, prebaked anode cells with automatic center-feed systems require that the alumina be consistent, with trouble-free handling properties to insure proper conveying and volumetric metering from the feeder. These criteria are best met by a free-flowing, moderate- to low-calcined alumina with relatively coarse and narrow particle size distribution.

Cell Gas Dry Scrubbing. The use of dry scrubber systems employing cell-feed alumina as adsorbent for fluorides in effluent gas from the cells dictates other requirements for metallurgical alumina:

- High adsorption capacity for hydrogen fluoride. This property is closely related to the specific surface area of the alumina, which is higher for the lower calcined aluminas.

- Attrition resistance.

- Free flowability.

- Higher chemical purity to compensate for capture in the dry scrubber of impurities which are recycled to the cell.

Pot Room Working Conditions. Use of low-calcined, high surface area alumina as a cover for the cell bath reduces fluoride evolution within the pot room. Working conditions in the smelter are degraded by dust caused by fine particles of alumina. Reduction of the fines fraction ($< 44 \mu\text{m}$) in the alumina and high attrition resistance are important for reducing dust.

Use of Stationary Calciners and Pneumatic Handling Systems for Alumina. The replacement of rotary alumina kilns by the energy-efficient stationary calciners has resulted in producing a different type of calcined alumina for smelter feed. This difference is reflected in the interrelationship between degree of calcination (measured by the mass loss on ignition), specific surface area, and the $\alpha\text{-Al}_2\text{O}_3$ content [143].

The strength of the alumina particles has become of concern not only because of relatively higher breakdown in the stationary calciners, but also because of attrition occurring in pneumatic unloading and conveying equipment and in fluid-bed dry-scrubbing systems. The generation of fine particles in such equipment, apart from causing unacceptable dusting conditions in the smelters, often results in troublesome segregation problems in alumina storage bins and bunkers.

Electrolyte Composition and Temperature. The trend to operating cells at lower temperatures with electrolyte having a lower bath ratio ($\text{NaF}:\text{AlF}_3$) has decreased the solubility and rate of dissolution of alumina in the electrolyte. The rate of dissolution is greater for aluminas having higher surface areas and low content of $\alpha\text{-Al}_2\text{O}_3$. Both properties can be achieved by a low degree of calcination.

Typical Specifications for Metallurgical Alumina

The considerations discussed above have contributed to the evolution of the general specifications used in production and international trading (Table 21.13). These values are only representative and considerable variation exists in actual practice depending on price, availability, smelting practices, and many other factors.

Table 21.13: Typical properties of metallurgical alumina.

Physical property	
Particle size distribution, %	
+ 100 mesh (Tyler)	< 5
+ 325 ($44 \mu\text{m}$)	> 92
- 325	> 8
Bulk density, kg/L	
loose	0.95-1.00
packed	1.05-1.10
Specific surface area, m^2/g	50-80
Moisture (to 573 K), %	< 1.0
Loss on ignition (573-1473 K), %	< 1.0
Attrition index (modified Forsythe-Hertwig method)	increase in $< 44 \mu\text{m}$ particles 4-15%
$\alpha\text{-Al}_2\text{O}_3$ content (by optical or X-ray method), %	< 20
Chemical analysis, %	
Fe_2O_3	< 0.020
SiO_2	< 0.020
TiO_2	< 0.004
CaO	< 0.040
Na_2O	< 0.500

21.10.1.6 Industrial Alumina Chemicals

Alumina, in various forms, is one of the inorganic chemicals produced in greatest volume today. Although production of aluminum metal currently consumes $\approx 90\%$ of all alumina, an increasing amount is being applied in the chemical industry for fillers, adsorbents, catalysts, ceramics, abrasives, and refractories. With the development and growth of applications and markets for alumina chemicals, all the major alumina producers have, over the years, converted a part of their capacity to produce various alumina chemicals. In fact, some of the older, smaller alumina refining plants have been totally converted to alumina chemi-

cals production in order to be economically viable. Chemical uses account for nearly 8% of the world production.

Aluminum Hydroxides

Aluminum hydroxides constitute a versatile group of industrial chemicals. Important uses requiring large quantities are as fillers in plastic and polymer systems and for the production of aluminum chemicals. A moderate amount is used for the production of alumina-based adsorbents and catalysts.

Aluminum hydroxide meets most of the requirements for an effective filler: white or near-white color; large volume production base, resulting in price and supply stability; consistency of physical and chemical properties; a wide range of particle size distributions chemical inertness; and nontoxicity. However, its increasing popularity as a plastics filler is strongly related to its fire-retardant and smoke-suppressant properties, which justify the somewhat higher price compared with calcium carbonate and other mineral fillers. Aluminum hydroxide acts as a fire retardant by adsorbing heat through endothermic dehydration and dilution of pyrolytically produced combustion gas by the released steam. Dehydration and water release processes become significant at temperatures above 500 K. The smoke-inhibiting activity of aluminum hydroxide filler has been attributed to promotion of solid-phase charring in place of soot formation. Although offering these desirable features, aluminum hydroxide has certain disadvantages that impose some limitations on its uses as a filler. Like other nonreinforcing mineral fillers, it generally lowers strength. Because it undergoes thermal decomposition, it is not suitable for processing above 500 K. These factors are responsible for the larger use of aluminum hydroxide in latex carpet backings and in glass-reinforced polyesters, where processing temperatures below about 480 K generally are used. These are also chemically cross-linked or fiber-reinforced systems, in which loss of strength caused by a nonreinforcing filler may not be very important. Alu-

minum hydroxide filler has been used less extensively in thermoplastics, e.g., poly(vinyl chloride) and polyethylene, and elastomeric materials. For use as a filler, the crystalline aluminum hydroxide from the Bayer process is dried and ground to particles $\leq 10\text{ }\mu\text{m}$ size. Special grades with increased whiteness and a variety of both particle size ranges and chemical purity also are available commercially.

Fine, precipitated aluminum hydroxide having a uniform particle size ($\approx 1\text{ }\mu\text{m}$) is used in paper making as a filler pigment and as a coating. As a filler, it disperses rapidly with low sedimentation. Improved printing properties are reported for the hydroxide-filled paper. The application of fine, platy aluminum hydroxide as a paper coating is well established in the paper industry. It gives a coating of high brightness, opacity, and gloss.

Technical aluminum hydroxide obtained from the Bayer process is 99.5% pure. It dissolves readily in strong acids and bases. For these reasons, aluminum hydroxide is the preferred raw material for the production of a large number of aluminum compounds. These include pure, iron-free aluminum sulfate (used in the paper industry and for water purification), aluminum fluoride, synthetic zeolites, and sodium aluminate. Aluminum hydroxide also is used in the glass industry and in cosmetic and pharmaceutical preparations. An important cosmetic use of aluminum hydroxide is in toothpaste. The mildly abrasive hydroxide cleans and polishes teeth.

The price of aluminum hydroxides ranged from \$0.20 to \$0.60 per kg in 1982, the price range reflecting the cost of additional processing of the usual Bayer process product to suit application requirements. These include grinding, higher purity, classification, surface treatment, etc. Pharmaceutical-grade gel hydroxides were at the top of the price range.

Adsorbent and Catalytic Aluminas

Activated aluminas represent another group of technically important alumina chemicals. Principal uses are as drying agents, adsorbents, catalysts, and catalyst carriers. These

products are obtained by thermal dehydration of different aluminum hydroxides in the 250–800 °C temperature range.

Preparation of Activated Aluminas

Bayer aluminum hydroxide is the chief source of commercial activated alumina products. Powder forms of activated alumina are produced by heating the hydroxide directly at 575–1825 K in ovens or in rotary or fluidized-bed calciners. The products have surface areas of 200–350 m²/g and losses on ignition of 3–12% (at 300–1200 °C). Such products are used as decolorizing agents for organic chemicals and as starting material for the production of aluminum fluoride. Other uses include chromatographic and catalytic applications in organic chemistry.

Granular activated alumina produced from Bayer plant crust is one of the oldest commercial forms of this product and still is used widely. A flow sheet of the production process is shown in Figure 21.34. The activated material is a hard, nondusting product. Table 21.14 lists some properties of a commercial product of this type (Alcoa F-1). A similar granular product has been produced by compacting Bayer hydroxide by mechanical pressure (Martinswerk GmbH, Germany). The process utilizes a roll-type compactor. The product from the compactor is broken up and sieved to the required size fractions and activated at 450–600 °C in a rotary calciner.

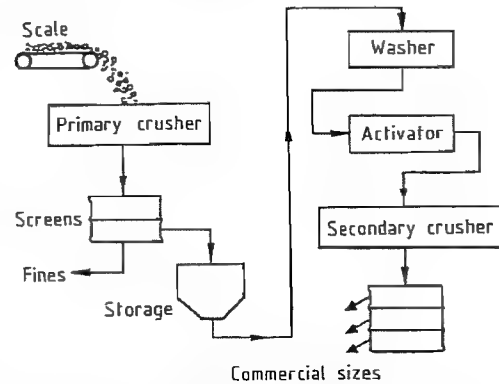


Figure 21.34: Flow sheet for production of activated alumina from Bayer plant crust.

Table 21.14: Typical properties of Alcoa activated aluminas.

	F-1	H-151	S-100
% Al ₂ O ₃	92	30	95
% Na ₂ O	0.58	1.6	0.35
% SiO ₂	0.12	2.0	0.03
% Fe ₂ O ₃	0.06	0.03	0.05
% LOI	7	6	5
Loose bulk density g/cm ³ lb/ft ³	0.83 52	0.82 51	0.80 50
Packed bulk density g/cm ³ lb/ft ³	0.85 55	0.85 53	0.75 47
Pore characteristics and surface area of typical Alcoa activated aluminas			
Helium (true) density, g/cm ³	3.25	3.40	3.15
Mercury (particle) density, g/cm ³	1.42	1.38	1.24
Micro pore volume (pores < 3.5 nm), cm ³ /g	0.017	0.023	0.012
Macro pore volume (> 3.5 nm), cm ³ /g	0.023	0.020	0.037
Total pore volume, cm ³ /g	0.40	0.43	0.49
Total porosity, %	56.3	59.4	60.6
Pore diameter at 50% total pore volume, nm	17.7	3.5	4.7
Primary pore size range, nm	0–10 000	0–40	0–500
BET surface area, m ² /g	250	360	260
Pore diameter, nm			
10 ⁶ –10 ⁷ Pore volume, cm ³ /g	0.0031	0.0003	0.0000
10 ⁵ –10 ⁶	0.0045	0.0001	0.0001
10 ⁴ –10 ⁵	0.0059	0.0001	0.0004
10 ³ –10 ⁴	0.0029	0.0004	0.0033
10 ² –10 ³	0.0045	0.0093	0.0047
35–10 ²	0.0021	0.0099	0.0289
2–35	0.0165	0.0232	0.0115
	0.095	0.0433	0.0489

Fast dehydration of Bayer aluminum hydroxide, either by vacuum or by exposure to high-temperature gas (780–1000 °C) for a few seconds, has been used for the production of ball-shaped, activated alumina having properties superior to the granular product. This process results in the formation of nearly amorphous α -Al₂O₃. The product is finely ground and using water as binder, formed into spherical agglomerates in a rotating pan agglomerator. Rehydration of α -Al₂O₃ with water leads to crystallization of bayerite, causing the agglomerates to harden. Reactivation of the hard balls at 400–500 °C produces the activated product (5–20 mm in diameter) having a surface area of 320–380 m²/g.

Alumina gels also have been used for the manufacture of activated aluminas. These gels are produced by neutralization of aluminum sulfate or ammonium alum by NH₄OH, or from sodium aluminate by neutralization with acids, CO₂, NaHCO₃, and Al₂(SO₄)₃. The ge-

latinous aluminum hydroxide precipitate is filtered and thoroughly washed and dried. The dried product is activated, milled, and agglomerated to a spherical product. Other forming processes, such as extrusion, pelletizing, and tableting, also can be used. The product is finally activated at 400–600 °C to a loss on ignition value of about 6%. Although gels of various textures can be prepared, the usual industrial adsorbent products have very small pores (less than 4 nm in diameter) and surface areas in the range of 300–400 m²/g. A flow sheet of a manufacturing process is shown in Figure 21.35. Table 21.14 reports data on a commercial, gel-based product (Alcoa H-151).

Aluminum oxide hydroxide (boehmite), a by-product from the Ziegler process for linear alcohol production, is another source of activated alumina. The high purity of this material favors its use in catalytic applications. The fine particle boehmite is normally extruded to

various shapes. The material is claimed to serve as its own binder when peptized with glacial acetic acid. The extrudate is cut to the required size, dried, and activated at 500–600 °C. The surface area of the activated product is 185–250 m²/g. Commercial bayerite also has been used to produce activated alumina; the product is preferred in some catalytic applications.

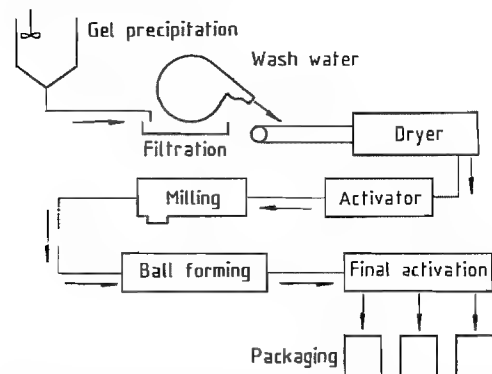


Figure 21.35: Production of gel-based activated alumina.

Adsorbent Applications

A major application of activated alumina is in the field of adsorption, where its high surface area, pore structure, strength, and chemical inertness favor its use. The alumina performs important technical functions, such as gas and liquid drying, water purification, and selective adsorption in the petroleum industry.

Gases that have been dried successfully by alumina desiccants are:

acetylene	ethylene	natural gas
air	freon	nitrogen
ammonia	furnace gas	oxygen
argon	helium	propane
carbon dioxide	hydrogen	propene
chlorine	hydrogen chloride	sulfur dioxide
cracked gas	hydrogen sulfide	
ethane	methane	

In many applications an alumina desiccant can dry gas to a lower dew point than any other commercially available desiccant. The static water adsorption capacities of two typical activated aluminas (Alcoa F-1 and H-151) in con-

tact with air at different relative humidity conditions are shown in Figure 21.36.

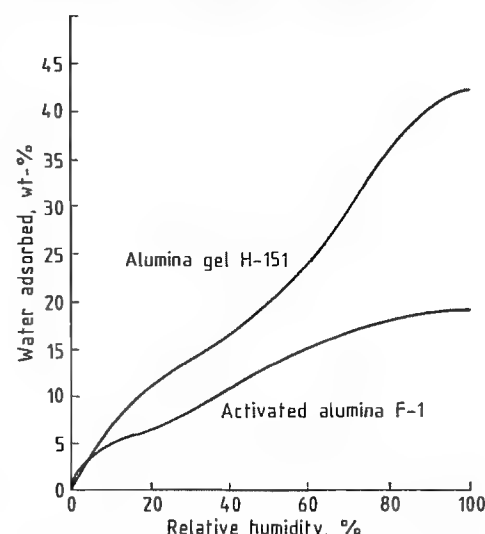


Figure 21.36: Static water adsorption capacity of typical commercial activated alumina at 25 °C.

Moist gas usually is dried by passing it through a column (or tower) packed with the adsorbent. Adsorption of water on activated alumina is strongly exothermic, releasing between 45 and 55 kJ of heat per mole of water adsorbed. This factor must be considered in the design of the drying tower. Both granular and spherical forms of activated alumina can be used in desiccant beds. Sizes from 2 to 20 mm are available commercially. The granular products have lower surface areas and their application is based on low cost per kilogram, low water load, and low stream pressure. Spherical products, produced by either the gel or the fast dehydration processes, have larger surface areas, a narrower pore structure, and a high adsorption capacity, and they are relatively more expensive than the granular variety. The spherical kind usually is specified for high-pressure, high-moisture removal duties. The alumina desiccant is regenerated by passing a current of hot, dry gas (200 °C) through the bed, usually countercurrent to the main gas flow.

Liquids that can be dried with activated alumina include aromatic hydrocarbons, higher

molecular mass alkanes, gasoline, kerosene, cyclohexane, power system coolants, lubricants, and many halogenated hydrocarbons. Liquids that are highly adsorbed on alumina (e.g., ethyl or methyl alcohol), react or polymerize in contact with activated alumina. Those containing components that tend to deposit on the alumina surface cannot be dried by activated alumina. Regeneration schemes for liquid dehydration units are varied and depend on the liquid being dried. In some applications the liquid being dried is vaporized, heated, and passed through the desiccant bed to desorb water. Hot, dry gases also are used for regeneration.

An evolving application of activated alumina is in water purification. Several important contaminants have been removed from water successfully and economically in pilot-plants as well as in large-scale treatment plants. These include reduction of fluoride concentration in drinking water and in some industrial effluents, and removal of color and odor from effluent water from dye works and paper plants. Removal of phosphate and arsenic also has been investigated.

Activated alumina can be used to separate one or more components from a gas or liquid stream by taking advantage of differences in adsorption or desorption kinetics. For example, a short cycle process has been used to recover heavy hydrocarbons from a stream of lighter hydrocarbons. Often a regeneration scheme can be devised that permits cyclic use of the alumina. In other instances, such as removal of catalyst in polyethylene and hydrogen peroxide production, it is more economical not to recycle the alumina.

Catalytic Applications

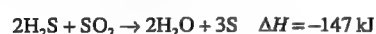
Alumina is used in many industrial catalytic processes, both as the catalyst and as a support for catalytically active components. In many instances, the alumina support contributes to catalytic activity and so assumes an essential role in the catalyst system. Other catalytic uses of alumina take advantage of its strength, heat resistance, and inertness.

Although the common adsorbent aluminas derived from Bayer hydroxide have many catalytic applications, high-purity materials (e.g., boehmite from the Ziegler process for linear alcohol production) are sometimes preferred. Because of the lower cost of Bayer process-based products, such techniques as water and acid washing of the activated product have been employed to reduce the alkali (Na₂O) content of the Bayer material. The sodium oxide is known to have a negative influence in many catalytic processes. Catalyst-forming methods include tableting, pelletizing, compacting, ball forming (agglomeration), and extrusion. Such factors as purity, surface area, pore volume, and size distribution, and rate of deactivation influence catalyst performance and selectivity. In addition, crushing strength and resistance to attrition of the catalyst pellets are important considerations in practical operation of catalytic reactors. Although these physical aspects of alumina catalysts are well characterized, the surface structure and chemistry responsible for catalytic activity still remains unclear. Many investigators have attributed catalytic activity to the intrinsic acidity of the surface of activated alumina. First, the combination of two neighboring OH⁻ groups to form water during the dehydration process leaves behind an exposed Al³⁺ ion, which, because of its electron deficiency, behaves as a Lewis acid site. In addition, hydroxyl groups are retained during thermal decomposition of aluminum hydroxide. These OH⁻ ions on the surface may act as proton-donors (Brønsted acids). These Lewis and Brønsted acid sites have been looked upon as the active catalytic centers. Further "defect" structures are formed with increasing degree of dehydration [144]. Of the types of defects created during dehydration, those assumed to have the greatest catalytic importance are the triplet vacancies. They provide unusual exposure of the aluminum ions in the underlying layer and constitute strong acid sites.

Catalytic applications of alumina are extensive. Important industrial processes employing alumina as a catalyst by itself include alcohol dehydration and the Claus process for

sulfur recovery. Dehydration of alcohols over activated alumina is one of the oldest catalytic processes. The products are olefins and/or ethers. Typical reaction conditions for olefin production are 300–400 °C and atmospheric pressure. Lower temperatures favor the formation of ethers. The most suitable aluminas for alcohol dehydration catalysis are those that have large surface areas (150–200 m²/g) and possess good thermal and hydrothermal stability. Coke formation occurs over a period of several hundred operating hours and the catalyst must be regenerated by burning off the carbon with hot air at 500–600 °C.

The largest present-day catalytic application of activated alumina itself is in the Claus process, which is used to recover sulfur from hydrogen sulfide (H₂S).



The reaction is carried out catalytically in two or more conversion stages using alumina catalysts. Reaction temperature in the first stage is around 350 °C. At this temperature, the conversion of H₂S is only about 65%. Subsequent lower temperature catalytic stages are used to further reduce the H₂S concentration. Spherical, high-strength activated alumina catalysts are used in the Claus converters. Service life as high as 5 years has been reported. Deactivation of the alumina catalyst occurs by sulfation, thermal aging, and carbon and/or sulfur deposition. Regeneration of Claus catalyst involves removal of sulfur and burning off of carbon deposits.

Alumina-supported catalysts are used extensively in the petroleum and chemical industries. In general, the petroleum industry catalysts have high surface area and high porosity; the support is mostly activated alumina. On the other hand, many typical chemical process catalysts (e.g., ammonia synthesis, steam reforming) are characterized by lower surface area (< 20 m²/g) and are non-porous or have very large diameter pores. The carrier in this case is inert and consists mostly of calcined or sintered alumina products.

Two different methods have been used commonly for preparation of alumina-supported catalysts: impregnation and coprecipitation. The alumina support used in the *impregnation process* generally has been formed into its final shape (extrudates, tablets) prior to the impregnation step. Impregnation with a salt solution of the active species is then carried out, followed by drying and thermal decomposition of the salt. In the *coprecipitation procedure*, hydroxides of aluminum together with the active component are precipitated from a salt solution by neutralization with ammonia or alkali. The washed precipitate is dried, powdered, and processed (e.g., by extrusion) to the desired shape and finally activated by thermal dehydration. The coprecipitation method is used when the active species must be present in high concentrations or when more uniform distribution of the active component is desired.

The technical and patent literature contains innumerable examples of the use of alumina as a catalyst support. Some important examples are the catalytic dehydration of *n*-butane to butadiene (used in synthetic rubber), using a chromia-impregnated alumina catalyst, cobalt molybdenum–alumina catalysts, used in hydrorefining operations (e.g., desulfurization) in petroleum refining; and pelleted catalysts containing platinum, palladium, and rhodium on an alumina base, used in automobile exhaust catalytic converters.

United States production of adsorbent-grade activated aluminas, both granular and spherical, amounted to nearly 250 000 t in 1980. Price of the cheaper, granular product was quoted around \$0.40–\$0.50 per kg. Price of the spherical product ranged from \$0.55 to \$0.65 per kg. Total catalytic applications of alumina in the United States were estimated to be around 400 000 t in 1980. Price of pre-formed alumina for catalytic applications ranges from \$0.60 to \$4.00 per kg, depending on source and purity. Alumina-based Claus catalyst was priced between \$3.00 and \$3.50 per kg.

21.10.1.7 Ceramic Uses of Alumina

Alumina is used extensively as a ceramic material. Products range from relatively low-calcined grades of polishing aluminas to the extremely hard, fused alumina and synthetically produced sapphire. The characteristics that make alumina valuable in ceramic applications are high melting point (2050 °C), hardness (9 on the Mohs scale), strength, dimensional stability, chemical inertness, and electrical insulating ability. These, together with availability in large quantities at moderate prices, have led to extensive and varied uses of alumina as a ceramic material.

Calcined Alumina

Ceramic aluminas are generally produced by calcining Bayer aluminum hydroxide at temperatures high enough for the formation of α-Al₂O₃. By control of calcination time and temperature and by the addition of mineralizers, such as fluorine and boron, the crystallite size in the calcined product can be varied from 0.2 to 100 μm. These calcined aluminas can be categorized broadly according to their sodium

content. There are two general types: those having about 0.5% Na₂O and low-soda grades with a content < 0.1%.

Reactive alumina is a material manufactured by dry grinding calcined alumina to particle sizes smaller than 1 μm. The large surface area associated with very fine particles and the high packing densities obtainable considerably lower the temperatures required for sintering.

Tabular aluminas are manufactured by grinding, shaping, and sintering calcined alumina. The thermal treatment at 1630–1880 °C causes the oxide to recrystallize into large, tabular crystals of 0.2–0.3 mm.

Fused Alumina

For ceramic applications and for the production of abrasives, fused aluminas are manufactured by melting a suitable raw material in an electric arc furnace. Calcined alumina from the Bayer process is used as a starting material for the highest quality fused alumina. Bauxites with varying levels of iron oxide, silicates, and titanium minerals are melted to produce the brown or less pure black qualities.

Table 21.15: Average annual net shipments by major markets in the United States.

Industry	Average annual net shipments, kt		Market distribution, %	
	1978–1982	1960–1964	1978–1982	1960–1964
Containers and packaging	1522	192	24.3	7.3
Building and construction	1241	666	19.8	25.3
Transportation	1115	549	17.8	20.8
Electrical	627	305	10.0	11.6
Consumer durables	436	284	6.9	10.8
Machinery and equipment	387	190	6.2	7.2
Other	277	229	4.4	8.7
Statistical adjustment	65	—	1.0	—
Domestic total	5670	2415	90.4	81.9
Exports	601	218	9.6	9.2
Total	6271	2633	100.0	100.9

Table 21.16: Solubility of aluminum sulfate as a function of temperature (grams of anhydrous salt per 100 g water).

t, °C											Reference
0	10	20	30	40	50	60	70	80	90	100	
31.3	33.5	36.15	40.36	45.73	52.13	59.10	66.23	73.14	80.83	89.11	[145]
31.2	33.5	36.4	40.4	46.1	52.2	59.2	66.1	73.0	80.0	89.0	[146]
27.5	27.6	28.0	28.8	29.9	31.0	31.8	36.6	38.74	46.85		[147]
23.9	25.0	26.9		31.5		36.4		41.7	47.0		[148]

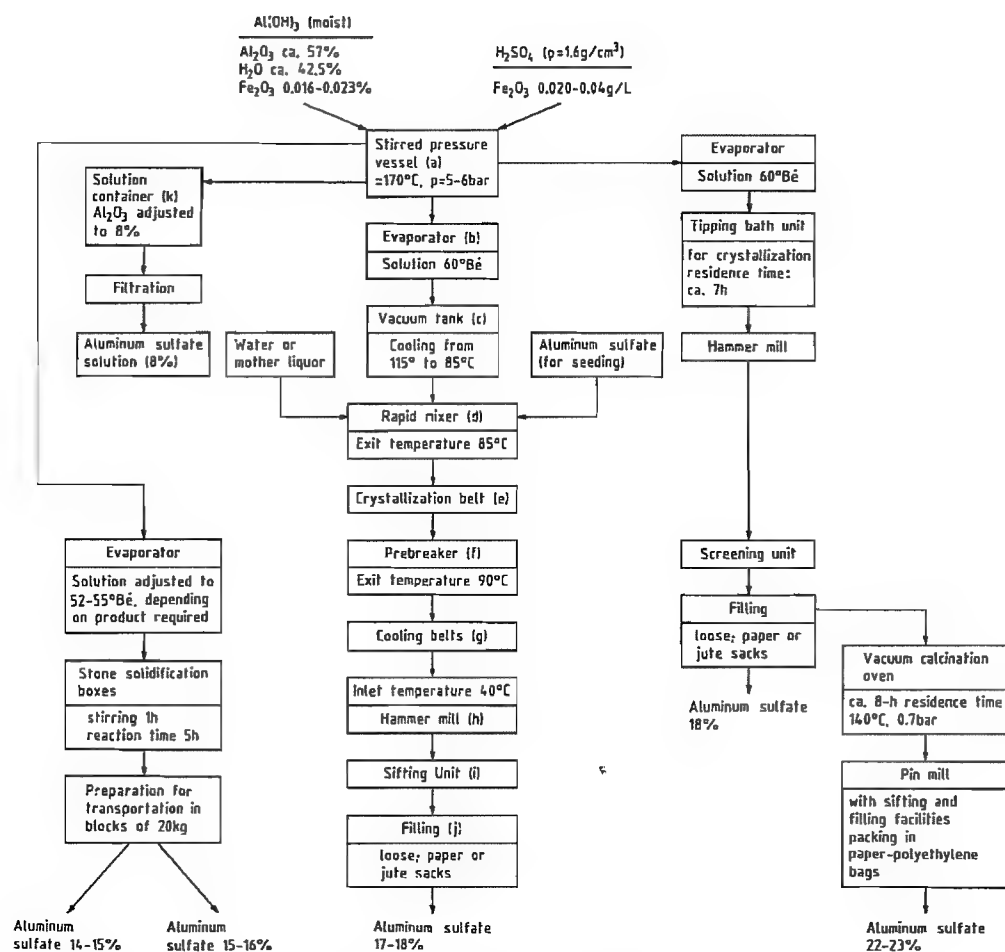


Figure 21.37: Production of aluminum sulfate by the Giuliani process [154].

21.10.2 Aluminum Sulfate and Alums

21.10.2.1 Aluminum Sulfate

Aluminum sulfate is the second most important industrial compound of aluminum, after aluminum oxide. Aluminum sulfate was first used in Paris in 1844 to replace potassium alum. Today, it has taken over almost all areas of application that potassium alum originally had.

Properties

Aluminum sulfate is almost insoluble in anhydrous alcohol but readily soluble in water; aqueous solutions are acidic. Literature data on solubility and the structure of the precipitate in water differ markedly and should be used with caution (Table 21.16). Previously, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was thought to crystallize from aqueous solution under normal conditions (20 °C, 1 bar). This is now doubted, because such factors as hydrolysis, oversaturation, shifts in equilibrium, and, particularly, poor crystal formation make definitive characterization difficult [149]. The

common form of aluminum sulfate, generally considered to be $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, occurs in nature as alunogen (hair salt) and can be crystallized from hydrochloric acid solution as microscopically small, white needles. However, some researchers ascribe a hydrate water content of 17 mol to this form of aluminum sulfate [150]. A hydrate containing 27 mol of water can be prepared readily and in high purity [145]. Other well-defined aluminum sulfates contain 16, 10, and 6 mol of water. A total of 39 basic and 3 acidic aluminum sulfates, as well as 13 different hydrates of the neutral salt, are described in the literature [151]. The existence of aluminum sulfates with 14, 13, 12, 9, 7, 4, 2, and 1 mol of water can be concluded from the vapor-pressure curves and the dehydration curves of the $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3\text{-Al(OH)}_3\text{-H}_2\text{O}$ systems [152, 153].

In industrial practice, the hydrate water content is unimportant because "crystalline" aluminum sulfate is a ground, microcrystalline solid with variable water content, which is obtained from a melt. The desired Al_2O_3 content is adjusted within certain limits by heating. At a temperature above 340 °C, anhydrous aluminum sulfate is formed, a white powder, ρ 2.71 g/cm³, that decomposes above 770 °C to aluminum oxide [153].

Production

In Germany and most European countries today, aluminum sulfate is produced on a large scale only from aluminum hydroxide and sulfuric acid by the Giuliani process. In this process, aluminum sulfate is obtained relatively easily with high purity. Production by the action of sulfuric acid on aluminum-containing ores (clays and bauxite with high silicon and low iron content, e.g., bauxite with $\text{SiO}_2 > 5\%$, Fe_2O_3 ca. 1%) is still important in some countries (Sweden, Spain, UK, USA, former USSR, Turkey, Venezuela) but to differing degrees.

Giulini Process [154]. The Giuliani method for producing various grades of aluminum sulfate, containing between 8 and 23% Al_2O_3 , is shown schematically in Figure 21.37.

A pressure-resistant, stirred vessel (a) is filled with aluminum hydroxide (moist or dry). The calculated quantity of warm sulfuric acid is added from a preheater, and the mixture is stirred. In calculating the sulfuric acid concentration required to obtain an SO_3 content of ca. 1% below stoichiometric, all process steps involving the introduction or the removal of water must be accounted for. Generally, acid of density 1.6 g/cm³ is used. The reaction starts after 60–300 s and is complete after 10–12 min. The heat of reaction causes the temperature to rise to ca. 170 °C, while the pressure rises to 5–6 bar. The mixture must not be stirred for more than 1 h because otherwise the aluminum sulfate can hydrolyze to give insoluble basic aluminum sulfate and strongly acidic sulfate melt. An autoclave unit allowing batches of 2.5 t can produce ca. 50 t of aluminum sulfate in a 10-h shift.

The melt is led into a copper container where it is concentrated by flash evaporation (b). From the evaporator, the melt is sucked into a well-isolated vacuum tank (c), which is evacuated to the vapor pressure of the aluminum sulfate melt. This vacuum cooling avoids incrustation of the heat exchanger surfaces.

The melt falls from the vacuum container into the mixer, where it is seeded at 85 °C with 1–2% aluminum sulfate powder. The pulplike product reaches the "crystallization belt", a smooth heat-resistant trough-form rubber conveyor belt (e), and crystallizes there in ca. 30 min. Because of the high heat of crystallization, the material has a temperature of ca. 90 °C and cannot be broken to fine size in one step (f). It passes over aircooled conveyor belts until it has cooled to 40 °C after which it is ground (h) and sieved (i). The goods are filled (j) into paper or jute sacks or transported loose in silo cars. Aluminum sulfate with 17.2% Al_2O_3 produced in this way contains only 0.01% insoluble material; therefore, digestion of the aluminum hydroxide is almost complete. For transportation as a solution the Al_2O_3 content is adjusted to ca. 8% to avoid crystallization during transport.

Production from Bauxite. Finely ground bauxite (for example, 60% Al_2O_3 , 1.5% Fe_2O_3 , 1.6% TiO_2 , 3.0% SiO_2 , 32% H_2O) also can be used as starting material. In this case, 3 mol H_2SO_4 are charged onto 1 mol Al_2O_3 . The Fe_2O_3 component in bauxite is disregarded because the Al_2O_3 is only 97–98% digested and therefore sufficient sulfuric acid is available for production of aluminum sulfate containing 17.5% Al_2O_3 . The aluminum sulfate obtained by digestion of bauxite contains ca 0.5% Fe_2O_3 and ca. 2.2% insoluble residue.

Production from Less Pure Starting Materials. Acid digestion of predominately silicon-rich raw materials gives a solution of aluminum sulfate. The purity depends on the process and starting materials. Iron, which strongly interferes, is precipitated with calcium hexacyanoferrate(II) as Berlin blue (iron hexacyanoferrate(II)), with calcium sulfide as iron sulfide, or by hydrolysis as basic iron sulfate. For details, see [155]. The clear solution is decanted and sold as a liquid or concentrated to 61.5°Bé, allowed to solidify, and milled. The final product, which contains ca. 0.5% Fe_2O_3 and 0.1% insoluble material, is the technical grade. In addition, there is an iron-free grade having an Fe_2O_3 content of ca. 0.005%.

The Kretschmar process is used to produce very pure, iron-free aluminum sulfate by digestion of clay (for example, 40–43% Al_2O_3 , 53–56% SiO_2 , 2–4% Fe_2O_3) with sulfuric acid. The greater part of the impurities is removed and crystals are separated from the solution by stirring. The formation of colloids is avoided by using vacuum apparatus. Pure, large crystals of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (15.3% Al_2O_3) can be separated easily from the impure mother liquor by centrifuging [156]. The residue from the digestion process (SiO_2) can be converted with lime to calcium hydrosilicate, which increases the hardness of and also plasticizes lime mortar.

In a process developed by the U.S. Bureau of Mines, alcohol is used to reduce the viscosity of the oversaturated aluminum sulfate mother liquor [157].

Olin Mathieson Chemical Corp. developed an economical process for producing high-quality aluminum sulfate from the clay or waste shale of coal mines. Large crystals (1.5–3 mm) with iron contents of less than 0.03% are produced in a patented crystallizer [158]. A process for producing aluminum sulfate from alum-containing ores is given in [159].

Aluminum sulfate is produced from waste "red mud" (from the aluminum oxide industry) by suspending the mud in water and passing sulfur dioxide through the suspension until pH 2 is reached. After filtration and removal of the sulfur dioxide in vacuo to give a pH of 4.5–5.0, $\text{Al}(\text{OH})\text{SO}_3$ and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ precipitate. The precipitate is filtered and treated with sulfuric acid, whereby aluminum sulfate dissolves. [160].

Commercial Grades. Whereas $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ theoretically contains 15.3% Al_2O_3 , commercial grades of aluminum sulfate contain 14–15%, 15–16%, 17–18%, 18%, or 22–23% Al_2O_3 (Table 21.17). Generally, the aluminum sulfate containing 17–18% Al_2O_3 (water-soluble aluminum content, calculated as Al_2O_3) is used most frequently. The calculated hydrate water content of this aluminum sulfate is 13 mol. The commercial grade containing 17–18% Al_2O_3 is delivered also with various special qualities, such as low arsenic or low iron content.

Table 21.17: Commercial grades of aluminum sulfate.

Grade	Al_2O_3 , %	Fe_2O_3 , %	Insoluble material, %	Basicity ^a , %
8% (solution)	8	0.004	—	1
14–15%	14–15	0.006–0.008	0.04	0.1–1.0
15–16%	15.1–16.0	0.006–0.008	0.04	0.1–1.0
17–18%	ca. 17.2	<0.01	0.03	0.1–1.0
18%	ca. 18.0	<0.01	<0.03	0.8–1.5
22–23%	ca. 22.8	<0.02	ca. 0.03	1.0–1.8

^a Defined in text.

The *basicity* of the product is defined as the excess in Al_2O_3 over the stoichiometric SO_3 : Al_2O_3 ratio. The 17–18% Al_2O_3 grade has a basicity of 0.11%, i.e., the Al_2O_3 content exceeds the stoichiometric amount by 0.1–1%. Occasionally, the term "basicity" is de-

fined as the ratio % SO_3 to % Al_2O_3 . For commercial aluminum sulfate, this ratio is ca. 2.30, whereas the theoretical value is 2.35. This weakly basic aluminum sulfate has the advantage that it is less hygroscopic and therefore hardly affects either the metal parts of the apparatus during use or paper sacks during transport. Also, free acid damages cellulose fibers in the paper industry.

Uses

About two thirds of the total aluminum sulfate production is used for treating water. About one half of the total production goes into the paper industry (paper sizing, pH adjustment wastewater purification) [161, p. 246].

Paper Industry. Aluminum sulfate is used for precipitating and fixing sizing agents, wet-strength agents, and basic dyes; for improving retention; for dispersing resin particles that stick together and block sieves; as the starting material of a high-quality slip for coating glossy paper (satin white); and for the production of lake dyes and wallpaper. For an overview of uses in newspaper factories, see [162]; for a detailed discussion on the importance of aluminum sulfate in paper production, see [149]. Aluminum sulfate with more than 0.2% Fe_2O_3 gives paper a yellow tinge and cannot be used for good-quality white paper.

Water Purification. Aluminum sulfate is an important flocculating agent for purifying water [163]. The mechanism is as follows: Positively charged aluminum ions, which are hydrated or hydroxylated with water via numerous intermediate stages, neutralize the negative charge on the colloidal material in the water. As a result of mutual adsorption, the material flocculates, sediments at various rates, and finally settles as sludge after 15–150 min. To neutralize the hydrogen atoms formed on hydrolysis of aluminum sulfate, some carbonate hardness is consumed:



For 50 mg/L of the 17–18% Al_2O_3 grade 0.25 mmol/L of carbonate hardness (based on

alkaline-earth ions) is consumed. Generally, 5–50 g aluminum sulfate is sufficient to purify 1 m³ of water. An advantage of using aluminum sulfate is the lack of postflocculation, provided the correct amount is added. Disadvantages are the formation of free carbon dioxide, the increase of noncarbonate hardness, such as calcium sulfate, and the pH remaining between 5 and 7. If no natural bicarbonate hardness is present, an alkaline substance that also has a dispersing effect, such as lime or sodium aluminate, must be added. Aluminum sulfate, used in combination with calcined leached clay, is suitable for binding mercury ions, for example, in sea water [164].

Other Uses. Aluminum sulfate with a very low iron content (below 0.01%) is used as a mordant in dyeing; a higher iron content is unacceptable because this leads to color changes. Further uses are for pickling of seeds, deodorizing of mineral oils, tawing, and producing aluminum hydroxide gel employed, for example, as a filler for synthetic rubber. Aluminum sulfate has some importance also as a catalyst support. Finally, it is the starting material for almost all other aluminum compounds.

Production and Capacity Data. Aluminum sulfate production in the United States was 1 168 000 t in 1980 and 1 075 000 t in 1982 [165]; that in Japan was 757 000 t in 1980 [166]. The main U.S. producer of aluminum sulfate is Allied Corp. The main Japanese producers are Nikkei Kako Co. and Scintoma Aluminum Smelting Co.

21.10.2.2 Alums

Historical Aspects. *Alumen*, from which the word alum is derived, was known to the ancient Greeks and Romans as an astringent and also as a mordant in dyeing wool. Alum was employed in processing skins, for embalming animal and human corpses, and for fireproofing wood. However, what was known at first as alum was not a defined substance but referred to both alum-containing minerals and mixtures of alum with iron vitriol. PARACELSUS was the first to distinguish true alum from iron

vitriol. In the years 1776–1798, CHAPTAL and VAUQUELIN established that alum was a double salt of potassium and aluminum sulfates and that the potassium ions could be replaced by ammonium ions. The raw material of the ancient alum industry was alum stone (alunite) or alum shale. Alum stone contains all components of the alum in the correct ratios and is processed by roasting and leaching. Roasting, aging for several years, and leaching of alum shale gave an aluminum solution from which the alum was precipitated with alkali. The alum industry played an important role during the whole of the Middle Ages.

The industrial production of the alums ceased to have particular importance when it became possible to produce aluminum sulfate economically in high purity, because only the aluminum content is of practical importance. Most of the alum production methods now have only limited, partly only historical, interest. Clay and other alkali-containing silicates, particularly bauxite, were used as raw materials and were digested using alkali or acid. Today, alums are produced only from aluminum hydroxide, which is obtained by the Bayer process from bauxite.

General Properties. Alums are crystalline double salts of the general formula (cation 1)⁺ (cation 2)³⁺(anion²⁻)₂·12H₂O. The most useful alums are those with trivalent aluminum cations and sulfate anions, M⁺Al³⁺(SO₄)₂·12H₂O. The individual components of the alum can be replaced, retaining both the regular crystalline form and the hydrate water. Alums with the following trivalent metals are known: iron, chromium, cobalt, manganese, titanium, vanadium, gallium, indium, scan-

dium, rhodium, and iridium. The monovalent component can be an alkali metal, or it can be ammonium, alkylammonium, arylammonium, or thallium. The existence of a lithium alum is uncertain. Known combinations include potassium–aluminum, cesium–aluminum, potassium–chromium, and hydroxyammonium–aluminum. A selenate alum also is known: KAl(SeO₄)₂·12H₂O.

All alums crystallize in strongly refracting octahedra or cubes [145]. They have an astringent taste and rot-proofing, protein-precipitating properties.

In *aqueous solution*, alums show all the chemical properties that their components show separately. Physical properties, such as color, electrical conductivity, and freezing-point lowering, are the sum of the properties of the components, provided the solutions are very dilute. At higher concentrations, complexes, such as [Al(SO₄)₂·(H₂O)₂]⁺, are formed. The solubilities of the alums in water decrease from sodium to cesium (see Table 21.18). On heating, the alums lose their water of crystallization either partially or completely. However, part of the water is taken up again at normal temperature and humidity.

Potassium Aluminum Sulfate

Potassium aluminum sulfate, known as potassium alum, KAl(SO₄)₂·12H₂O, ρ 1.75 g/cm³, and ammonium aluminum sulfate are the aluminum compounds known longest. Potassium alum occurs in nature as efflorescence on alum shale and in volcanic areas on trachyte and lava as feather alum.

Table 21.18: Solubility of some aluminum alums as a function of temperature (grams of anhydrous salt per 100 g water).

<i>t</i> , °C	0	10	20	30	40	50	60	70	80	90	100
Sodium	56.2	60.5	61.5	66.7							
Potassium	3.0	4.0	5.9	7.9	11.7	17	25	40	71	109	154
Ammonium	2.6	4.5	6.6	9.0	12.4	15.9	21.1	26.9	35.2	50.3	70.8
Rubidium	0.71	1.09	1.40		3.1	4.98			21.6		
Cesium	0.2	0.3	0.4		0.8	1.24			5.3		22.8
Thallium	3.05	4.4	6.2		12.6		26.0				

Potassium alum crystallizes in large, colorless, transparent octahedra, which melt at 92.5 °C in their own water of crystallization. The hardness of the crystals on the Mohs scale is 2. The octahedra absorb long-wavelength IR radiation almost completely, but are transparent to visible light. Certain substances (hydroxides, carbonates, borates, carbamides, also metals and organic dyes) promote the formation of basic aluminum sulfate by binding free sulfuric acid in the mother liquor. Under these conditions, the cubic form is favored (cubic or Roman alum).

Potassium alum is stable in air of normal humidity. Dehydration does not begin below 30 °C, but at 65 °C nine moles of water are lost. Literature data on the dehydration are contradictory. Recent investigations on thermal decomposition are given in [167]. According to these results, K₂SO₄, γ -Al₂O₃, and 3K₂SO₄·Al₂(SO₄)₃ form at 780 °C, whereas K₂SO₄, α -Al₂O₃, and K₂O·12Al₂O₃ are produced at 1400 °C. When heated above its melting point, potassium alum dehydrates, forming calcined alum (alum ustum), KAl(SO₄)₂. At red heat, SO₃ is released.

Potassium alum is soluble in dilute acid but almost insoluble in anhydrous alcohol, acetone, and methyl acetate. Because of the marked increase in solubility in water with temperature, potassium alum can be purified more easily than other aluminum salts by recrystallization and, in particular, can be freed from iron sulfate. Mixed crystals form readily with ammonium sulfate.

Basic potassium aluminum sulfate, K[Al(OH)₂]₃(SO₄)₂·³/₂H₂O, occurs in nature as löwigite. The compound is made synthetically as a rather insoluble, amorphous powder by heating aluminum sulfate, water, and an excess of potassium sulfate or by heating potassium alum with water in the ratio 1:4 to 200 °C [168]. Another basic potassium aluminum sulfate, K[Al₃(OH)₆(SO₄)₂], containing less water, is the alum stone (alunite) occurring in nature.

Production. Aluminum hydroxide (wet hydrate; Al₂O₃ ca. 57%, Fe₂O₃ 0.016–0.023%,

H₂O 42.5%) and sulfuric acid ($\rho \approx 1.6$ g/cm³; Fe₂O₃ 0.020–0.040 g/L) react in a stirred, corrosion-resistant pressure boiler at 5–6 bar to form aluminum sulfate as shown in Figure 21.37. The aluminum sulfate melt is then led, with release of pressure, into a copper container. Here, a stoichiometric quantity of potassium sulfate (as chloride-free as possible) is added. The solution is heated to ca. 100 °C for 2–3 h and adjusted to 40–44 °Bé with mother liquor. After filtration from insoluble material, the alum melt is left in crystallization boxes for 10 days, after which the alum is removed in blocks. The product obtained in this way contains < 0.001% Fe₂O₃, 0.001–0.004% chloride, and < 0.01% insoluble material.

For the production of *alum crystals*, the alum melt is brought into a stirred crystallization bath, where it is cooled to ca. 40 °C by air bubbles. The pulp is then separated from the mother liquor by centrifuging and washed. The mother liquor is collected and returned to the copper container. The potassium alum is dried at 50–60 °C. The salt, which forms lustrous crystals, is sieved and packed in paper bags that are lined with polyethylene.

A process for obtaining potassium alum from alum-containing ores is given in [159], and the production of basic potassium and sodium alums from synthetic alum is described in [169].

Uses. As already mentioned, the industrial importance of potassium alum has declined considerably. However, it is still employed in tawing skins, as a mordant in dyeing, and as a coagulating agent for latex. Because of its astringent and protein-precipitating properties, potassium alum is used in the pharmaceutical and cosmetics industries. The use of potassium alum as a styptic pencil, because of its blood-stanching property, is very widespread and popular. The most important application today is in the gypsum industry, which employs potassium alum as hardening agent and setting accelerator for the production of marble cement and alabaster plaster. However, for purifying water and sizing paper, potassium alum has been replaced completely by alumi-

num sulfate. In the paper industry, aluminum sulfate is designated traditionally, although incorrectly, as an alum.

Ammonium Aluminum Sulfate

Ammonium aluminum sulfate, also called ammonium alum, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, ρ 1.64 g/cm³, mp 93.5 °C, occurs in nature as shermigite. Crystals doped with other alums show birefringence. The solubility of ammonium alum in water is similar to that of potassium alum, with which it forms a continuous series of mixed crystals. Ammonium alum is slightly soluble in dilute acids and glycerol but insoluble in absolute alcohol. In aqueous solution, ammonium alum is neutral.

Data on loss of water on heating are in disagreement. GEL'PERIN and CHEBOTKEVICH [170] have reported that water of crystallization is released in three stages: first to give the hydrate with 21 mol water, then to that with 3 mol water and finally to the anhydrous product, so that it is in fact more correct to formulate ammonium alum with 24 mol water. Above 193 °C, decomposition with the release of ammonia begins. On glowing above 1000 °C, sulfur trioxide is lost, leaving an aluminum oxide residue.

Production. Ammonium alum is made today mainly by dissolving aluminum hydroxide in sulfuric acid and adding ammonium sulfate but sometimes by the reaction of ammonia gas with aluminum sulfate and sulfuric acid. The procedure is analogous to the potassium alum process. To obtain a quality particularly low in iron oxide or other metal oxides (< 0.0001 % Fe_2O_3 ; normal quality ca. 0.001 % Fe_2O_3), as is required for production of synthetic gems, very pure starting materials must be used. Ammonium alum occurs as an intermediate in the "aloton" process, which operates in a sulfuric acid medium. This process had some importance prior to 1945 in Germany and the United States for aluminum hydroxide and aluminum oxide production.

Uses. In Europe, ammonium alum is not used in large quantities. Applications include those

in dressing furs in tanning, in the production of very fine aluminum oxide particles for polishing metallographic surfaces, and, in some countries outside Europe, as a disinfectant. In the United States, ammonium alum is important as an additive in baking powder; ca. 500 t/a are produced for this purpose. More recently, ammonium alum has gained considerable importance as starting material for the production of the finely powdered, loose aluminum oxide of high purity that is required for synthesizing corundum gems, such as rubies and sapphires. This quality of aluminum oxide is made by heating ammonium alum (or ammonium aluminum selenate alum) to 1000 °C.

Sodium Aluminum Sulfate

Sodium aluminum sulfate, sodium alum, $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, melts at 61 °C in its water of crystallization. In nature, it occurs as the mineral mendozite. Again, the data on thermal dehydration disagree. Sodium alum is insoluble in absolute alcohol but is much more soluble in water than all other alums. Alum powder (very fine crystalline form) is not available commercially. These two facts make it difficult to obtain sodium alum free from iron. Because of this and also because of its strong tendency to age, sodium alum has never gained the same importance as the other alums. In Europe, its use has been abandoned. In the United States, however, sodium alum is still utilized in relatively large quantities (ca. 3000 t/a) in baking powder.

Production. In the United States, sodium alum is produced by adding a clear solution of sodium sulfate to aluminum sulfate. After dilution to 30 °Bé and subsequent heating, a sludge of potassium sulfate, sodium silicate, and caustic soda is added to improve the purity of the product. The mixture is pumped into a stirred vessel, where it is mixed for several hours. During this stage, the ratio of aluminum sulfate to sodium sulfate is adjusted to the stoichiometric amount. Afterwards, the melt is pumped into an evaporator and concentrated to such an extent that it solidifies to a hard cake on pouring into a cooling tank. This so-

dium alum cake is then heated and finally ground to the desired size (99% through a sieve of 100 mesh) [161, p. 250].

21.10.3 Aluminates

Only the aluminates of barium and sodium have importance in industry. Aluminates occur also in cement and in spinels.

21.10.3.1 Sodium Aluminate

Sodium aluminate is an important commercial inorganic chemical. It functions as an effective source of aluminum hydroxide for many industrial and technical applications. Commercial grades of sodium aluminate are available in solid and liquid forms. Pure sodium aluminate (anhydrous) is a white crystalline solid having a formula variously given as NaAlO_2 , $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$, or $\text{Na}_2\text{Al}_2\text{O}_4$. Commercial grades, however, always contain more than the stoichiometric amount of Na_2O , the excess being on the order of 1.05 to 1.50 times the formula requirement. Hydrated forms of sodium aluminate are crystallized from concentrated solutions.

Sodium aluminate has no defined melting point; it softens above 1700 °C when sodium begins to evaporate slowly, leaving aluminum oxide.

Production. The chief commercial process for the manufacture of sodium aluminate is the dissolution of aluminum hydroxides in sodium hydroxide solution. Aluminum trihydroxide (gibbsite) from the Bayer process can be dissolved in 10–30% aqueous NaOH solution at a temperature near the boiling point.

The use of more concentrated NaOH solutions leads to a semisolid product. The process is carried out in steam-heated vessels of nickel or steel, and the aluminum hydroxide is boiled with ca. 50 % aqueous sodium hydroxide until a pulp forms. After this is poured into a tank and cooled, a solid mass containing about 70 % NaAlO_2 is formed. After being crushed, this product is dehydrated in a rotary oven heated either directly or indirectly by burning hydrogen. The resulting product contains ca.

90% NaAlO_2 and 1 % water together with 1 % free NaOH. The solubility of the salt produced in this way depends strongly on how much excess sodium hydroxide is used.

Alternatively, bauxite can be used directly as the alumina source. Bauxites containing gibbsite are extracted at 150 °C and 5 bar, whereas boehmite containing bauxite requires higher temperatures (230 °C) and pressures. The sodium aluminate solution obtained from the digestion process is separated from any impurities and then concentrated to the commercial liquid grade by evaporation. The solid product is obtained by drying the liquid.

The sinter method also has been used to produce sodium aluminate. By sintering sodium carbonate directly with Bayer aluminum trihydroxide in rotary sintering kilns at 1000 °C, an essentially anhydrous product can be obtained. When sintering bauxite, it is essential to leach the sinter mass with water and separate the impurities.

Uses. The major use of sodium aluminate is for water treatment, including both potable and industrial waters. Sodium aluminate is used as an adjunct to water softening systems, as a coagulant aid to improve flocculation, and for removing dissolved silica. Sodium aluminate dissolves in water to give a solution that has a pH value of 8. The aluminum hydroxide that precipitates from this solution has excellent flocculation properties and coagulates other impurities present in the water. Depending on the impurities, the conditions of precipitation can be improved by adding aluminum sulfate [171].

In *construction technology*, sodium aluminate is employed to accelerate the solidification of concrete, mainly when working during frost, under water, and in humid soil (Table 21.19). Compared to calcium chloride, which acts in a similar manner, sodium aluminate has the advantage of greater setting acceleration at low water-to-cement ratios [172]. Because it does not attack the reinforcing metals, it can be used for work with steel-reinforced concrete. Too rapid setting can cause cracks in the concrete, affecting the final strength of the

building. By adding substances such as oxoacids [173], sugar, naphthene [174], K_2CO_3 , or Na_2SO_4 [175] the final strength increases without affecting the setting rate significantly. Sodium aluminate increases the resistance of mortar to water, alkali, and acid. For the production of expanded concrete, sodium aluminate serves to activate nitrogen-releasing substances [176]. To stabilize foam formation in the production of light refractory bricks, up to 5% (relative to the total dry mass) sodium aluminate is added.

Table 21.19: Acceleration of setting by sodium aluminate in a mixture of 6 parts sand, 2 parts concrete, and 1 part water.

% $NaAlO_2$ in concrete	Setting started	Setting completed
0	4 h 30 min	6 h
1	30 min	1 h 40 min
1.5	15 min	30 min
2	10 min	15 min
10	instantly	

Increasingly, sodium aluminate is being used for the production of *synthetic zeolites*, used as catalyst supports or as catalysts [177–180] and as adsorbents. Sodium aluminate is one of the principal sources of *alumina* of the preparation of alumina adsorbents and catalysts.

In the *paper industry*, sodium aluminate increases the opacity [181], retention of fibers and filling materials [182], and the paper strength [183]. Also, it stabilizes the pH value of the water circulation [184] and increases the dispersion stability of titanium dioxide [185].

Another application of sodium aluminate is as a *pickle* to protect metallic surfaces (copper [186], aluminum [187], among others). This effect is based on the formation of a thin, very firmly adhering layer of aluminum hydroxide or, after heat treatment, of aluminum oxide on the surface, which does not affect the metallic luster. In the *enamel industry*, sodium aluminate is added to enamel mixtures to achieve low-melting covers [188].

Further applications of sodium aluminate are in lithography for the production of printing inks [189] and print forms [190], in the de-

tergent and varnish industries, in the production of water-insoluble floor waxes [191], as a dispersion agent for production of high-purity asbestos [192], as an additive to drilling fluids [193], and in the textile industry as a mordant in dyeing and in printing cloth. Many other uses of sodium aluminate have been reported. These include inhibition of glass etching by alkaline solutions; protection of steel surface during galvanizing; improving dyeing, antipiling, and antistatic properties of polyester synthetic fibers; as an additive to foundry sand molds and cores; and as a binder in the ceramics industry.

21.10.3.2 Barium Aluminates

The industrially important barium aluminates are $BaO \cdot 6Al_2O_3$, *mp* 1915 °C; $BaO \cdot Al_2O_3$, *mp* 1815 °C; and $3BaO \cdot Al_2O_3$, *mp* 1425 °C [194]. The first two crystallize hexagonally.

Barium aluminates are produced by melting bauxite with coal and barite. Leaching the melt gives a solution of barium aluminate, from which the salt is obtained by evaporation. Very pure barium aluminates can be produced by sintering mixtures of aluminum oxide with barium carbonate. All barium aluminates, including such hydrated compounds as $BaO \cdot Al_2O_3 \cdot 4H_2O$, $2BaO \cdot Al_2O_3 \cdot 5H_2O$, $BaO \cdot Al_2O_3 \cdot 7H_2O$, and $7BaO \cdot 6Al_2O_3 \cdot 36H_2O$, hydrolyze in water, forming hydrargillite (gibbsite), $Al(OH)_3$, and relatively soluble barium hydroxide.

Barium aluminate is used for purifying water because the Ba^{2+} ion precipitates both the sulfates and the carbonates, whereas the aluminate ions form insoluble calcium aluminate. A further use of barium aluminates is as a special cement, for example, as binding agent for the production of high-temperature refractories, and in the production of radiation shields [195].

21.10.4 Aluminum Alkoxides

Aluminum alkoxides (alcoholates) are solid or liquid compounds of covalent character.

They are readily soluble in hydrocarbons, but sparingly soluble in alcohols. Hydrolysis with water occurs readily, giving aluminum hydroxide and the corresponding alcohol. For a general review of aluminum alkoxides, see [196]. Industrially, only the isopropoxide (isopropylate) and *sec*-butoxide (*sec*-butylate) are important. These compounds are used to adjust the viscosity of varnishes, to impregnate textiles, as intermediates in the production of pharmaceuticals, and as antitranspirants in cosmetics. In the industrial production of ketones and aldehydes, aluminum alkoxides are employed as reducing agents (Meerwein-Ponndorf reaction).

Aluminum iso-propoxide, $Al(OCH(CH_3)_2)_3$, is a white solid, *mp* 118 °C, *bp* 125–130 °C at 533 Pa, d_4^{20} 1.0346, flash point 26 °C. It is usually produced by direct reaction of aluminum and isopropyl alcohol in the presence of mercury(II) chloride catalyst. In a later version of the process [197], the alcohol was heated under reflux in a column filled with aluminum chips; no catalyst was required and nearly quantitative conversion was obtained. The alkoxide can be purified by distillation. In an alternative production method, excess isopropyl alcohol is added to a solution of aluminum chloride in benzene; the hydrogen chloride formed is removed by introducing dry ammonia into the reactor and filtering off the ammonium chloride that precipitates.

Aluminum sec-butoxide, $Al(OC_4H_9)_3$, is a colorless liquid, *bp* 180 °C at 533 Pa, d_4^{20} 0.9671, flash point 26 °C, and is produced in a manner similar to aluminum isopropoxide.

21.10.5 Aluminum Chloride

21.10.5.1 Anhydrous Aluminum Chloride

ØRSTED first prepared anhydrous aluminum chloride in 1825 by the reaction of chlorine gas with a mixture of alumina and carbon. This compound has acquired great significance in organic chemistry as a catalyst, particularly for Friedel–Crafts syntheses and

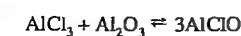
allied reactions for the production of alkylated aromatics, dyestuffs, pharmaceuticals, and perfumery chemicals. For general literature, see [145] and [198].

Properties

Physical Properties. In the solid and gas phases at temperatures up to 400 °C, aluminum chloride is present as the dimer, Al_2Cl_6 . Dissociation of the dimer progresses with rising temperature and is quantitative above 800 °C. Solid aluminum chloride crystallizes to form a monoclinic layer lattice. Pure aluminum chloride is white, but the commercial product usually has a yellowish or grayish tinge because of small amounts of iron chloride or aluminum impurities. Physical properties of anhydrous aluminum chloride [199]:

ρ at 25 °C	2.44 g/cm ³
Sublimation temperature at 101.3 kPa	181.2 °C
Triple point, at 233 kPa	192.5 °C
Heat of formation at 25 °C	−705.63 ± 0.84 kJ/mol
Heat of sublimation of dimer at 25 °C	115.73 ± 2.30 kJ/mol
Heat of fusion	35.35 ± 0.84 kJ/mol
Heat of solution at 20 °C	−325.1 kJ/mol

Chemical Properties. Anhydrous aluminum chloride reacts extremely violently with water, evolving hydrogen chloride. The hexahydrate, $AlCl_3 \cdot 6H_2O$, is formed in this reaction. In aqueous solution, aluminum chloride is partially hydrolyzed to hydrochloric acid and aluminum oxychloride, $AlClO$. For this reason, anhydrous aluminum chloride cannot be obtained by concentrating the solution and calcining the hydrate. When aluminum chloride is heated with γ -alumina, aluminum oxychloride, $AlClO$, forms, but this reaction goes in the reverse direction at temperatures above 700 °C:



If aluminum chloride vapor is passed at 1000 °C under reduced pressure over molten aluminum, volatile aluminum monochloride, $AlCl$, is formed, but this decomposes immedi-

ately into the elements in cooler zones of the reactor. This method has been adopted for purifying aluminum.

Reaction between aluminum chloride and other metal halides, such as CaCl_2 , CrCl_3 , and FeCl_3 , gives mixed halides. Eutectic melts with other metal chlorides are of industrial significance, for example, that with sodium chloride is used as a solvent in chlorination reactions.

Anhydrous aluminum chloride dissolves readily in polar organic solvents. As a Lewis acid it forms addition compounds with numerous electron donors, such as hydrogen chloride, hydrogen sulfide, sulfur dioxide, sulfur tetrachloride, phosphorus trichloride, ethers, esters, amines, and alcohols.

Production

The starting materials are either aluminum or pure aluminum oxide. Bauxite now has no economic significance as a raw material because of the iron chloride always present in the product.

Chlorination of Aluminum [200]. Today, most anhydrous aluminum chloride is made by chlorinating aluminum.

Chlorine is passed through molten aluminum in ceramic-lined, tube-shaped reactors. The reaction is highly exothermic:



The temperature in the reactor is maintained at 670–850 °C by controlling the admission rates of chlorine and aluminum and by cooling the reactor walls with water. The aluminum usually is replenished in the form of lumps. The difficulty of controlling the large heat of reaction can be overcome also by dividing the process into a number of small units.

The aluminum chloride vapor leaving the reactors is passed through ceramic-lined tubes into large air-cooled iron chambers. Solid aluminum chloride is withdrawn from the condenser walls at regular intervals, ground (insuring exclusion of moisture), and classified by sieving. Chlorine in the off-gas is re-

moved by conventional methods such as absorption in caustic soda solution.

Chlorination of Pure Aluminum Oxide. Chlorination of alumina is advantageous over the formerly widely used bauxite process (less reactor corrosion and higher-purity product), and at the same time it avoids the high raw material costs involved in metal chlorination [201].

Carbon monoxide and chlorine are partially converted to phosgene over an activated charcoal catalyst. The gaseous reaction mixture enters a brick-lined, fluidized-bed reactor, where it reacts with finely divided γ -alumina to yield aluminum chloride. The reaction is exothermic enough (ca. 300 kJ/mol, based on AlCl_3) to maintain the temperature at 500–600 °C without external heat. Consequently, the process permits large units, and the low reaction temperature insures that the brick lining has a long life.

The aluminum chloride vapor is filtered through a bed of coarse pumice chips, condensed, and further processed described above. The off-gas contains chlorine, phosgene, and large amounts of carbon dioxide. The chlorine is removed by scrubbing, and the phosgene is hydrolyzed with water. Extremely pure aluminum chloride is obtained by resublimation from molten sodium aluminum chloride.

Quality Specifications and Analysis

Anhydrous aluminum chloride is ground and marketed as powder or granules. Aluminum usually is determined by complexometry; the chloride, by argentometry. The assay is 98–99% AlCl_3 . The main impurity is iron (0.05% max. or 0.01% for resublimed product). Sampling and analysis of anhydrous aluminum chloride must be carried out in an atmosphere of dry air or nitrogen.

Handling, Storage, and Transportation

Because of its corrosive and irritant action, anhydrous aluminum chloride is classified as a

dangerous substance. National and international regulations must be observed, such as 67/548/EEC, the key European Economic Community directive dealing with the classification, packaging, and labeling of dangerous substances.

Handling. Goggles, gloves, and protective clothing must be worn when handling aluminum chloride. A fume cupboard or a respirator with filter type B/St against acid gases should be used. Because hydrogen chloride is evolved when aluminum chloride is exposed to water, any spills must be taken up dry, and only small, residual amounts can be washed away with plenty of water. Sodium bicarbonate or slaked lime should be used for neutralization.

Storage and Transportation. Aluminum chloride is dispatched in vented steel drums or in tank trucks or rail tankcars that can be emptied pneumatically with dry air or nitrogen (dew point below –40 °C). Because the product tends to cake, it should not be stored for more than six months. International marine transportation is governed by the IMDG code, class 8, UN no. 1726. RID, ADR, ADN: Class 8, no. 11b, Rn 801, 2801, 6801, respectively. EEC: Yellow Book 78/79, EG no. 013-003-00-7. United Kingdom: Blue Book, Corrosives & IMDG code E 8031. United States: DOT regulations, corrosive solid, CFR 49, 172.101.

Uses

Anhydrous aluminum chloride is an important *Friedel–Crafts catalyst* in the chemical and petrochemical industries [202, 203]. A principal application is the alkylation of benzene by alkyl halides to form alkylbenzenes that are consumed in the production of synthetic detergents, such as alkylbenzene-sulfonates. Aluminum chloride also catalyzes the liquid-phase ethylation of benzene with ethylene to yield ethylbenzene, most of which is used in the production of styrene.

Ethyl chloride is produced mainly by the reaction of hydrochloric acid and ethylene in

the presence of aluminum chloride; the consumption has significantly decreased because of the declining demand for tetraethyl lead as an antiknock additive.

In the dyestuffs industry, aluminum chloride is widely used as catalyst in the production of anthraquinone and its derivatives and of pigments, such as phthalocyanine green. A further application of aluminum chloride is as a finish for titanium dioxide pigments, which are in this way protected from oxidation by an oxide layer.

Until 1960, aluminum chloride was used extensively in petroleum refining for cracking and isomerization, but it has now been replaced by zeolite catalysts. It is still employed in reforming hydrocarbons, as a polymerization catalyst in the production of hydrocarbon resins, and for the production of butyl rubber.

It is a catalyst also in the production of compounds, such as aromatic aldehydes, ketones, and 2-phenyl-ethanol, used in fragrances. Other applications for anhydrous aluminum chloride include the production of aluminum borohydride, lithium aluminum hydride, as well as compounds of phosphorus and sulfur.

Most of these reactions with aluminum chloride produce a solution that is often used as a flocculating agent in the treatment of waste water.

Aluminum chloride also is an intermediate in the production of aluminum by the Alcoa smelting process [204].

Data on the consumption of anhydrous aluminum chloride in the United States are given in Table 21.20.

Table 21.20: United States anhydrous aluminum chloride consumption in 1993 (not including the amounts consumed in the production of aluminum) [205].

Alkylate detergents	2 200 t
Ethylbenzene	4 000 t
Hydrocarbon resins	3 900 t
Pharmaceuticals	4 000 t
Titanium dioxide	2 200 t
Miscellaneous	4 900 t
Total	21 200 t

21.10.5.2 Aluminum Chloride Hexahydrate

Properties. The white hydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ crystallizes hexagonally and dissolves exothermally in water (133 g hexahydrate per 100 g water at 20 °C) [206]. The solubility increases only slightly with temperature. The aqueous solutions are strongly acidic because the salt hydrolyzes. Hydrogen chloride is evolved on heating concentrated solutions. The structure of aqueous solutions of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ is discussed in [207].

Production and Uses. Aqueous solutions of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ can be obtained by dissolving aluminum hydroxide in hydrochloric acid: the hexahydrate crystallizes when hydrogen chloride passes into cold (about 20 °C) saturated solution. In this way, impurities, particularly iron(III) chloride, can be removed [206]. Aluminum chloride hexahydrate has only minor importance as such; for example, it is used for hardening photographic layers. However, it is of industrial importance as an intermediate in the production of aluminum oxide [208, 209].

21.10.5.3 Basic Aluminum Chlorides

Properties. Basic aluminum chlorides, aluminum hydroxychlorides, aluminum chloride hydroxides, poly(aluminum hydroxychlorides), have the general formula $\text{Al}_2(\text{OH})_{6-n}\text{Cl}_n \cdot x\text{H}_2\text{O}$. The individual compounds are best defined either by the molar ratio of aluminum to chloride ($^{2/}_n$) or by their basicity, defined as $(1 - \frac{n}{6}) \times 100\%$. Below a minimum water content, which depends on n , the compounds are unstable; they decompose to aluminum hydroxide and aluminum oxide on heating to above 80 °C, releasing water and hydrogen chloride. All basic aluminum chlorides with $n = 1-5$ can be isolated, and all are white, in some cases crystalline substances, partially soluble in the lower alcohols [210, 211], but readily soluble in water. For example, 170 g of the compound $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2.5\text{H}_2\text{O}$ dissolves in 100 g water at 20 °C. However, the viscos-

ity of the solution prevents further amounts from dissolving. The *electrical conductivities* of the aqueous solutions, shown in Figure 21.38, are characteristic of the basic aluminum chlorides.

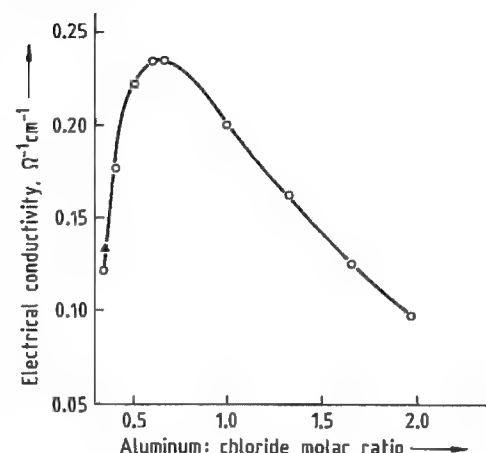


Figure 21.38: Electrical conductivity of freshly prepared basic aluminum chloride solutions: \circ from Locron L (ca. 50% aqueous solution of $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2.5\text{H}_2\text{O}$) and hydrochloric acid at constant aluminum oxide concentration (11.5%) and 20 °C; \blacktriangle prepared directly from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

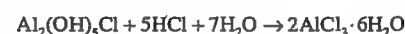
Table 21.21: pH values of aqueous solutions of $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2.5\text{H}_2\text{O}$ at 20 °C (mass fractions, w , in %).

w	pH
60	3.4
30	4.0
15	4.2
10	4.3
5	4.4
3	4.4

Aqueous solutions of basic aluminum chlorides are acidic because the compounds hydrolyze (Table 21.21). The stability of the solutions depends on the basicity: compounds with aluminum to chloride molar ratios of ca. 0.5:1 to about 1.6:1, corresponding to basicities of ca. 30–75%, decompose to give insoluble basic aluminum chloride at a rate that depends on the temperature and concentration of the solution [212]. On the other hand, compounds of basicity greater than 75% are very stable in aqueous solution. For example, compounds with the approximate composition $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2-3\text{H}_2\text{O}$ are so stable at concen-

trations > 50% that no decomposition occurs, even on boiling for days.

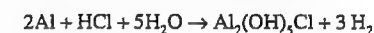
In contrast to the aluminum chlorides of low basicity (below 65%), the compounds of high basicity (above 65%) do not crystallize from their aqueous solutions, but form glassy masses. When solutions in the basicity range 30–65% are evaporated, the compound $\text{Al}_2(\text{OH})_{3.7}\text{Cl}_{2.3} \cdot 6.05\text{H}_2\text{O}$ (basicity 62%) always crystallizes [213]. On addition of alkali to basic aluminum chlorides, aluminum hydroxide precipitates. Hydrochloric acid converts all basic aluminum chlorides to the hexahydrate:



Chemical Structure. Basic aluminum chlorides have been known for a long time [145, p. 205], but only recently have investigations given significant insight into their chemical structures [214–217]. Basic aluminum chlorides are mixtures of complex compounds of various degrees of polymerization. Spectroscopic and kinetic investigations of the basic aluminum chlorides and of their solutions [214–218] lead to the conclusion that the complex ion $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ is present and is in equilibrium with its polymeric forms. Variations observed in the properties of these aqueous solutions such as viscosity and pH are caused by polymerization and depolymerization [219, 220].

Analysis. Basic aluminum chlorides are so stable that the aluminum content can be determined only after decomposition of the complex ion [221, 222]. The usual procedure is to mix the solution containing aluminum with 60% sulfuric acid and 0.1 M disodium ethylenediaminetetraacetate, followed by ca. 20% sodium hydroxide. The pH is adjusted to 4.7–4.9 at 60–70 °C. After the solution is cooled to about 25 °C and buffer solution (acetic acid, ammonium acetate), acetone, and indicator (dithizone in ethanol) are added, the solution is back-titrated with 0.1 M zinc sulfate. One milliliter of 0.1 M disodium ethylenediaminetetraacetate is equivalent to 2.698 mg of aluminum.

Production. Basic aluminum chlorides are made by dissolving either aluminum hydroxide or metallic aluminum in hydrochloric acid. Aged aluminum hydroxide leads only to compounds of basicity up to 65% [212]. To obtain aluminum chlorides of high basicity, freshly precipitated aluminum hydroxide [223] must be used. However, the preferred method is to dissolve aluminum in hydrochloric acid either thermally or electrochemically:



This method is exemplified by the following process [224]:

Aluminum electrodes are set up at distances of 40 mm in a corrosion-resistant electrolysis cell. Hydrochloric acid (ρ 1.04 g/cm³) is poured into the cell at a rate such that the reaction temperature remains at ca. 80 °C. After all the hydrochloric acid has been added, the voltage between the first and last electrodes is set so that an average voltage of 0.6 V per electrode pair is obtained at a current density of ca. 170 A/m². The formation of explosive gas mixtures must be avoided throughout the reaction by diluting the hydrogen with air or nitrogen to below the explosion limit. After about 70 h, the density of the electrolyte increases to about 1.2–1.3 g/cm³, and the pH value to about 3.5. At the same time the cell voltage fails. The electrolyte then consists of a solution containing aluminum and chloride in the molar ratio 2:1, corresponding to a basicity of 83%. The corresponding bromides as well as iodides are obtained by the same method. The solid halides are obtained from the solutions by careful evaporation or by spray drying [225]. Recently, another method may be of interest: controlled thermic decomposition of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ [226].

Uses and Quality. The scope of applications for basic aluminum chlorides has increased considerably in recent years. The most important basic aluminum chloride has the composition $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2-3\text{H}_2\text{O}$. Very stringent purity specifications apply to this substance. The maximum levels permitted are Fe 100 ppm, SO_4 500 ppm, Pb 20 ppm, As 3 ppm. These are required for its chief application,

namely, that in the cosmetics industry as the effective component of antiperspirants [227, 228]; trade names are Chlorhydrol (Reheis, USA), Locron (Hoechst, Germany), and Wickenol (Wickhen, USA). Other areas of application for this aluminum chloride are in the production of catalysts and highly temperature-resistant fibers based on Al_2O_3 , as a hydrophobic agent for impregnation of cotton textiles, for tanning leather, as a retention agent in paper production, as a binding agent for fire-resistant ceramic products, and as a hardening agent for rapid fixing baths in the photographic industry. Aluminum chlorides of low and moderate basicities, often known collectively as poly(aluminum chloride), are used particularly in flocculation chemicals for the treatment of water [229, 230]. For example, trade name of one of such a substance is Povimal (Hoechst).

21.10.6 Toxicology

Aluminum sulfate is classified as nontoxic; an LD_{50} value of 6207 mg/kg (mouse, oral) is reported [231]. Alum solutions are known for their astringent (tissue-contracting) effects. A TLV of 2 mg/m³ was established for water-soluble aluminum salts [232].

Anhydrous aluminum chloride has a corrosive and irritant effect on the skin, respiratory tract, and eyes. The toxic effect is caused by the evolution of hydrochloric acid when the product is exposed to moist air. The resulting respiratory difficulties vary from mild irritation to coughing. The MAK value (1995) and TLV (1983) for hydrochloric acid are both 7 mg/m³ [232, 233].

The extensive use of the *basic aluminum chloride* $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2-3\text{H}_2\text{O}$ in the cosmetic industry worldwide over more than 30 years has shown that this compound is not irritating to the skin in the concentrations used commercially. Although intermittent application of 150 mg $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2-3\text{H}_2\text{O}$ over a period of 3 days was found to cause mild skin irritation in humans, a dose of only 7.5 mg of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ caused the same degree of irritation [234].

21.10.7 Aluminum Benzoate

$\text{Al}(\text{C}_6\text{H}_5\text{O}_2)_3$, a crystalline powder, is slightly soluble in water. Aluminum benzoate is used as a stabilizer in poly(vinyl chloride).

21.11 Pigments

21.11.1 Ultramarine Pigments

Blue ultramarine (blue from over the sea) is the name which European artists of the Middle Ages gave to the pigment derived from lapis lazuli a semiprecious stone imported mainly from Afghanistan. Ultramarine was the supreme blue of medieval times, but eventually it became scarce and very expensive.

In 1828, J. B. GUIMET in France and CHRISTIAN GMELIN in Germany independently devised similar processes for synthetic preparation. Relatively abundant supplies soon became available, the price fell dramatically, and ultramarine was adopted as a general-purpose color.

Synthetic ultramarines are inorganic powder pigments, commercially available in three colors:

- Reddish blue, C.I. Pigment Blue 29:77007
- Violet, C.I. Pigment Violet 15:77007
- Pink, C.I. Pigment Red 259:77007

A green variety, once produced in small quantities, is no longer available.

Within limits set by stability considerations, the proportions of the chemical constituents can vary. The typical lattice repeat unit of a blue ultramarine is $\text{Na}_{6.9}\text{Al}_{5.6}\text{Si}_{6.4}\text{O}_{24}\text{S}_{4.2}$. The violet and pink variants differ from the blue mainly in the oxidation state of the sulfur groups. This is reflected in somewhat lower sodium and sulfur contents.

21.11.1.1 Chemical Structure

Reviews of work on the structure of ultramarine are given in [235, 236].

Ultramarine is essentially a three-dimensional aluminosilicate lattice with entrapped sodium ions and ionic sulfur groups (Figure 21.39). The lattice has the sodalite structure,

with a cubic unit cell dimension of ca. 0.9 nm. In synthetic ultramarine derived from China clay by calcination, the lattice distribution of silicon and aluminum ions is disordered. This contrasts with the ordered array in natural ultramarines.

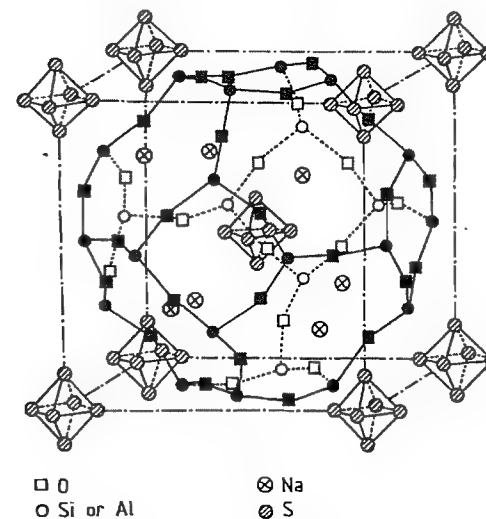


Figure 21.39: Schematic drawing of the basic structure of standard ultramarine showing the available sites for sulfur and sodium.

In the simplest ultramarine structure, equal numbers of silicon and aluminum ions are present and the basic lattice unit is $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ or $(\text{Na}^+)_6(\text{Al}^{3+})_6(\text{Si}^{4+})_6(\text{O}^{2-})_{24}$ with a net ionic charge of zero as required for structural stability.

The nature of the sulfur groups responsible for the color is reviewed in [237–239]. There are two types of sulfur group in blue ultramarine, S_3^- and S_2^- , both being free radicals stabilized by lattice entrapment. In the predominant S_3^- species, the spacing between the three sulfurs is 0.2 nm and the angle between them is 103°. S_3^- absorbs a broad energy band in the visible green-yellow orange region centered at 600 nm, while S_2^- absorbs in the violet-ultraviolet region at 380 nm (Figure 21.40).

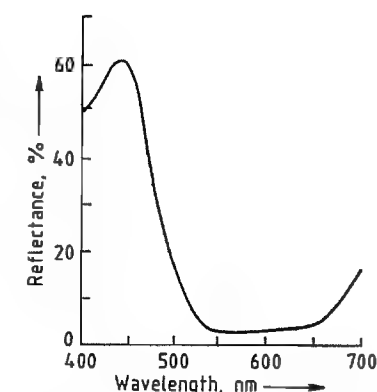


Figure 21.40: Spectral reflectance distribution of blue ultramarine.

The basic lattice $(\text{Na}^+)_6(\text{Al}^{3+})_6(\text{Si}^{4+})_6(\text{O}^{2-})_{24}$ is derived from $\text{Si}_{12}\text{O}_{24}$ by substituting six of the silicon ions by aluminum. Every Al^{3+} must be accompanied by a Na^+ so that the overall ionic charge for the structure is zero. Hence, six of the eight sodium sites are always filled by sodiums required for lattice stability and the remaining two sites are filled with sodiums associated with ionic sulfur groups. This means that only one S_3^- polysulfide ion can be inserted into the lattice (as Na_2S_3) even though subsequent oxidation to S_3^- leads to loss of one of the accompanying sodium ions. This gives a basic ultramarine lattice formula of $\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$.

To increase the sulfur content and thereby improve color quality, the lattice aluminum content can be decreased by including a high-silicon feldspar in the manufacturing recipe. This reduces the number of sodium ions needed for lattice stabilization and leaves more for sulfur group equivalence. A typical product would be $\text{Na}_{6.9}\text{Al}_{5.6}\text{Si}_{6.4}\text{O}_{24}\text{S}_{4.2}$ with a stronger, redder shade of blue than the simpler type.

In violet (Figure 21.41) and pink (Figure 21.42) ultramarines, the lattice structure is little changed, but the sulfur chromophores are further oxidized, possibly to S_3Cl^- , S_4 , or S_4^- .

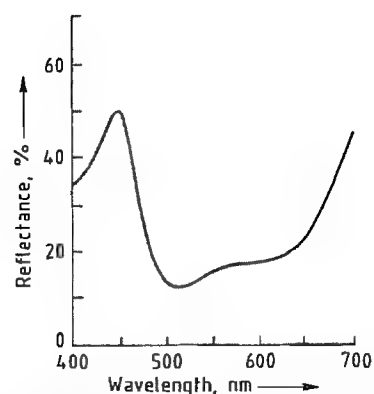


Figure 21.41: Spectral reflectance distribution of violet ultramarine.

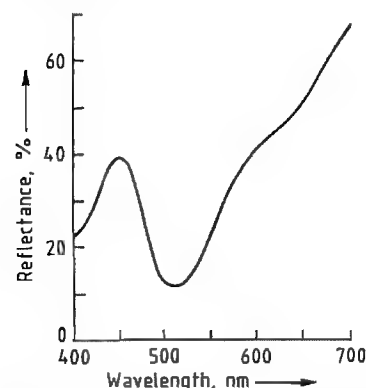


Figure 21.42: Spectral reflectance distribution of pink ultramarine.

Ultramarines are zeolites, though lattice paths are restricted by 0.4 nm diameter channels. The sodium ions can be exchanged for other metal ions (e.g., silver, potassium, lithium, copper). Although this produces marked color change, none of the products have commercial value.

21.11.1.2 Properties

The basic ultramarine color is a rich, bright reddish blue, the red-green tone varying with chemical composition. The violet and pink derivatives have weaker, less saturated colors (see Figures 21.40–21.42, for reflectance spectra).

The color quality of commercial pigments is developed by grinding to reduce particle

size and thus enhance tinting strength. Mean particle size ranges typically from 0.7 to 5.0 μm . Figure 21.43 shows an electron micrograph of a 1.0 μm grade. Fine pigments are lighter in shade and rather greener than coarser grades, but when reduced with white, their color is brighter and more saturated.

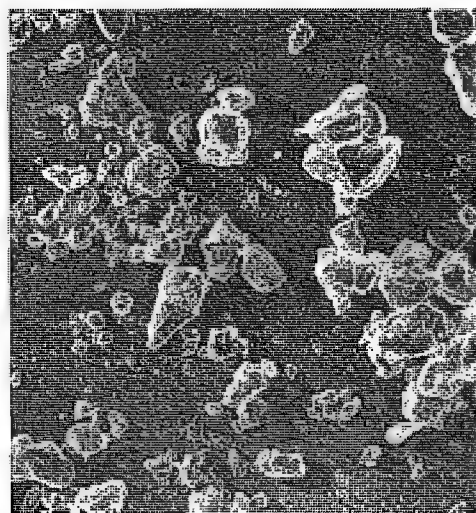


Figure 21.43: Electron micrograph of blue ultramarine with a mean particle size of 1.0 μm (magnification $\times 5800$).

With a refractive index close to 1.5, similar to that of paint and plastics media, ultramarine gives a transparent blue in gloss paints and clear plastics. Opacity is obtained by adding a small quantity of a white pigment. Increasing quantities of white give paler shades, and a trace of ultramarine added to a white enhances the whiteness and acceptability.

In many applications ultramarine blue is stable to around 400 °C, violet to 250 °C, and pink to 200 °C. All have excellent lightfastness with a 7–8 rating (full and reduced shades) on the International Blue Wool Scale. Color fade attributed to light exposure or moderate heat is almost always caused by acid attack. Ultramarines react with all acids, and if there is sufficient acid, the pigment is completely decomposed losing all color to form silica, sodium and aluminum salts, sulfur, and hydrogen sulfide. Evolution of hydrogen sulfide with acids is a useful test for ultramarine.

Grades resistant to transient acidity are available, in which the pigment particles are protected by a coating of impervious silica. Blue and violet grades are stable in mildly alkaline conditions, but pink tends to revert to a violet shade.

Ultramarines are insoluble in water and organic solvents, so the color does not bleed or migrate from paints or polymers.

Being macromolecular, the fine ultramarine particles have a high surface energy and are cohesive. The finer grades, with their greater surface area, are therefore less easy to disperse than the coarser types, and some are available with pigment surfaces treated to reduce energy and improve dispersibility.

Ultramarines adsorb moisture on the external particle surfaces and at the internal surfaces of the zeolite structure. External surface moisture (1–2% according to particle size) is driven off at 100–105 °C, but the additional 1% of internal moisture needs 235 °C for complete removal.

Ultramarine particles are hard and can cause abrasion in equipment handling either dry or slurried pigment.

Specific gravity is 2.35, but bulk density of the pigment powder is much lower, varying with particle size between 0.5 and 0.9 g/cm³.

Oil absorption also varies with particle size (usually 30–40 g%). The pH lies between 6 and 9. Ultramarine pigments are largely odorless, nonflammable, and do not support combustion.

21.11.1.3 Production

Ultramarine is made from simple, relatively cheap materials, typically china clay, feldspar, anhydrous sodium carbonate, sulfur, and a reducing agent (oil, pitch, coal etc.). Use of a synthetic zeolite has been proposed [240, 241], but this method is not known to be in commercial use.

Clay Activation. The clay is heated to about 700 °C to destabilize the kaolinite structure by removing hydroxyl ions as water. This can be either a batch process with the clay in crucibles in a directly fired kiln, or a continuous

process in a tunnel kiln, rotary kiln, or other furnace.

Blending and Heating Raw Materials. The activated clay is blended with the other raw materials and dry-ground, usually in batch or continuous ball mills, to a mean size approaching 15 μm . Typical recipes (in %) are:

	Green-tone	Red tone
Calcined clay	32.0	30.0
Feldspar		7.0
Sodium carbonate	29.0	27.0
Sulfur	34.5	33.0
Reducing agent	4.5	3.0

The ground mixture is heated to about 750 °C under reducing conditions, normally in a batch process. This can be done in directly fired kilns with the blend in lidded crucibles of controlled porosity, or muffle kilns. The heating medium can be solid fuel, oil, or gas. The sodium carbonate reacts with the sulfur and reducing agent at 300 °C to form sodium polysulfide. At higher temperatures the clay lattice reforms into a three-dimensional framework, which at 700 °C is transformed to the sodalite structure, with entrapped sodium and polysulfide ions.

Oxidation. The furnace is allowed to cool to ca. 500 °C when air is admitted in controlled amounts. The oxygen reacts with excess sulfur to form sulfur dioxide, which exothermically oxidizes the di- and triatomic polysulfide ions to S_2^- and S_3^- free radicals, leaving sodium sulfoxides and sulfur as by-products. When oxidation is complete, the furnace cools and is unloaded a full kiln cycle can take several weeks. The "raw" ultramarine product typically contains 75% blue ultramarine, 23% sodium sulfoxides, and 2% free (uncombined) sulfur with some iron sulfide.

Purification and Refinement. The purification and refinement operations can be batch or continuous. The raw blue is crushed and ground, slurried in warm water, then filtered and washed to remove the sulfoxides. Reslurrying and wet grinding release the sulfurous impurities and reduce the ultramarine particle size, often to 0.1–10.0 μm . The impurities are floated off by boiling or cold froth flotation.

The liquor is then separated into discrete particle size fractions by gravity or centrifugal separation; residual fine particles are reclaimed by flocculation and filtration. The separated fractions are dried and disintegrated to give pigment grades differentiated by particle size. These are blended to sales-grade standard, adjusting hue, brightness, and strength to achieve specified color tolerance.

Violet ultramarine can be prepared by heating a mid-range blue grade with ammonium chloride at ca. 240 °C in the presence of air. Treating the violet with hydrogen chloride gas at 140 °C gives the pink derivative.

A good ultramarine pigment would meet the following specification:

Tinting strength/standard	± 2 % max.
Reduced shade/standard	1 CIELAB unit max.
Free sulfur	0.05 % max.
Water-soluble matter	1.0 % max.
Sieve residue (45 µm)	0.1 % max.
Moisture	
coarse grade	1.0 % max.
fine grade	2.0 % max.
Heavy metals	traces

21.11.1.4 Uses

The stability and safety of ultramarine pigments are the basis of their wide range of applications which include the following:

Plastics
 Paints and powder coatings
 Printing inks
 Paper and paper coating
 Rubber and thermoplastic elastomers
 Latex products
 Detergents
 Cosmetics and soaps
 Artists colors
 Toys and educational equipment
 Leather finishes
 Powder markers
 Roofing granules
 Synthetic fibers
 Theatrical paints and blue mattes
 Cattle salt licks
 White enhancement

Plastics. Blue ultramarine can be used in any polymer; violet ultramarine has a maximum processing temperature of 250 °C, and pink ultramarine has a maximum processing temperature of 200 °C. With PVC, acid-resistant grades must be used if color fades during pro-

cessing. Surface-treated grades are available for enhanced dispersibility. Ultramarines do not cause shrinkage or warping in polyolefins. Ultramarine pigments are permitted worldwide for coloring food-contact plastics.

Paints. Ultramarine pigments are used in decorative paints, stoving finishes, transparent lacquers, industrial paints, and powder coatings. They are not recommended for colored, air-drying paints for outdoor use in urban atmospheres.

Printing Inks. Ultramarine pigments can be used in inks for most printing processes including hot-foil stamping. Letterpress, flexography, and gravure need high-strength grades; lithography needs water-repellent grades; any grade is suitable for screen inks, fabric printing, and hot-foil stamping.

Paper and Paper Coating. Ultramarine pigments are used to enhance the hue of white paper or for colored paper. They can be added directly to the paper pulp, or used in applied coatings. When added to the pulp, acid-resistant grades must be used if acid-sizing is employed. They are particularly suitable for colored paper for children's use.

Detergents. Ultramarine pigments are widely used to enhance the effects of optical brightening agents in improving whiteness of laundered fabrics [242]. They do not stain or build up with repeated use.

Cosmetics and Soaps. Ultramarine pigments are widely used in cosmetics. Pink is not recommended for toilet soaps because of the color shift to violet. Advantages are complete safety, nonstaining, and conformance to all major regulations.

Artists' Colors. This traditional use for ultramarine in all types of media is still an important application. Unique color properties, stability, and safety are highly prized.

Toys and other Articles/Materials for Children's Use. Ultramarine pigments are widely used in plastics and surface coatings for toys, children's paints and finger paints, modeling compositions, colored paper, crayons, etc.

They comply with major regulations and standards.

21.11.1.5 Toxicity and Environmental Aspects

Ultramarines are safe in both manufacture and use. Their only known hazard is the evolution of hydrogen sulfide on contact with acid. Massive exposure of workers in well over a century of manufacture, worldwide use for whitening clothes, and use in a number of countries for whitening sugar have all been without reported ill-effects.

Tests sponsored by Reckitt's Colours confirm that acute oral toxicity in rats and mice (LD_{50}) is greater than 10 000 mg/kg. Fish toxicity (LC_{50} in rainbow trout) exceeds 32 000 mg/L. Ultramarine is nonmutagenic, nonirritant, and nonsensitizing to skin.

There is no listed threshold limit value or maximum exposure limit for the pigment. Normal practice is to consider it a nuisance dust with TLV 10 mg/m³. The pigment is not listed as a dangerous substance in the EC nor in any similar national or international classification; neither is it classified as hazardous for disposal.

The production process evolves close to 1 t of gaseous sulfur dioxide and 0.3 t of water-soluble sodium sulfoxides for every tonne of pigment produced. These must be disposed of in an environmentally acceptable manner. If the soluble salts are fully oxidized, they can be discharged safely into tidal waters. Future legislation in all producing countries may require removal of sulfur dioxide from the effluent gases before discharge to the atmosphere.

21.11.1.6 Economic Aspects

Ultramarines can be categorized as either laundry grades, which are low-strength and

sometimes low-purity materials, or as industrial grades, which are high-strength, high-purity pigments.

Factories in several countries produce laundry-grade materials, including several in China, India, Eastern European countries, and one in Pakistan. Neither the numbers of these units nor their outputs are accurately known.

There are only three major producers of high-grade ultramarine pigments – Daiichi Seika (Japan), Nubiola (Spain), and Reckitt's Colours (France, United Kingdom) – with two smaller producers in Austria and Colombia. In 1990 total worldwide production was ca. 20 000 t/a.

21.11.2 Aluminum Phosphate

Commercial aluminum phosphate anticorrosive pigments consist of aluminum zinc phosphate hydrates [243, 244], or zinc-containing aluminum triphosphate [245]. Their compositions and properties are listed in Table 21.22. Aluminum zinc phosphate hydrate pigments are produced by reacting acid solutions of aluminum hydrogen phosphate with zinc oxide and alkali aluminate. The precipitated pigment is filtered off from the mother liquor, washed, dried, and ground [246]. Commercial aluminum triphosphate pigments contain ions of trimeric phosphoric acid which form stable aluminum-containing iron phosphate complexes [245].

The aluminum phosphate pigments give good adhesion of the paint film to the metallic substrate.

Trade names are as follows:

Zinc aluminum phosphate: K-White 105 (Teikoku Kako, Japan); Heucophos ZPA (Dr. H. Heubach, Germany); Phosphinal PZ04 (SNCZ, France).

Aluminum triphosphate: K-White 82, -84 (Teikoku Kako, Japan).

Table 21.22: Composition and properties of aluminum phosphate anticorrosive pigments.

Property	Aluminum triphosphate (commercial product 1; K-White 82) [245]	Aluminum triphosphate (commercial product 2; K-White 84) [245]	Aluminum zinc phosphate hydrate (commercial product 3; Heucophos ZPA, Phosphinal PZ 04) [243, 244]
Al content, %	5.5–7.7	4.7–6.9	4–5
Zn content, %	11.6–14.9	21.3–24.5	35–39
P ₂ O ₅ content, %	42.0–46.0	36.0–40.0	30/37
SiO ₂ content, %	13.0–17.0	11.0–15.0	
Loss on ignition (600 °C), %	ca. 10	ca. 8	10–16
Density, g/cm ³	3.0	3.1	3.2
Oil absorption value, g/100 g	35	30	30/35
Particle size, µm	0.5–10	0.5–10	0.5–10
pH value	6–7	6–7	6.5
Water-soluble content, %	max. 1.0	max. 1.0	0.1
Color	white	white	white

21.11.3 Production

Aluminum pigments are produced by grinding aluminum powder, usually obtained by atomizing molten aluminum. The starting material is mainly aluminum ingots with a purity of 99.5% (DIN 1712), or pure aluminum (> 99.95%) for special outdoor applications (acid-resistant grades).

Aluminum powder forms explosive mixtures with air; the lower explosive limit being ca. 35–50 g/cm³. Dust-free aluminum paste is therefore used in most applications.

Aluminum pigments are mainly produced by wet milling in white spirit. The resulting pigment suspension is usually fractionated, sieved, and filtered on a filter press. The filter cake is mixed with solvents to give the usual commercial consistency with 65% solids. Other solvents may be used instead of white spirit, the choice being governed by the intended application. The white spirit can be removed by vacuum drying and replaced by another solvent if necessary (e.g., for printing inks or coloring plastics).

Aluminum behaves as an amphoteric metal, liberating hydrogen from both alkaline and acid aqueous media. In waterborne paints and coloring systems, special stabilized aluminum pigments are therefore required [247]. Aluminum pigments must not be used with halogen-containing solvents because they re-

act very violently to release hydrogen halides (Friedel–Crafts reaction).

The leafing properties of aluminum pigments can be adversely affected by polar solvents or binders. "Leafing-stabilized" aluminum pigments are available for these applications.

Along with special pigments for modern environmentally-friendly coating systems (e.g., waterborne paints and powder coatings) described above, aluminum pigments coated with colored metal oxides (e.g., iron oxide) have appeared on the market which produce not only reflection but also interference effects [248]. Novel color effects are obtained by combining the metal-oxide-coated pigments with transparent colored pigments.

Aluminum has a very low toxicity and is permitted as a coloring agent (EEC no. E173, C.I. 77000). It is also approved by the FDA, § 175300 (USA).

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22 Titanium

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22.1 Introduction

Titanium, is a member of group 4 of the periodic table. It has two *4s* and two *3d* valence electrons and is a transition element. The electronic configuration is $1s^2 2s^2 p^6 3s^2 p^6 d^2 4s^2$. Natural titanium is a mixture of five stable isotopes [7]:

Mass number:	46	47	48	49	50
Abundance, %:	7.95	7.75	73.43	5.51	5.34

The following unstable isotopes also exist:

Mass number:	43	44	45	51
Half-life:	0.58 ± 0.004 s [8]	1000a	3.08 ± 0.06 h [9], [11], 72 ± 2 d [10]	6 min

22.2 History

In 1791, GREGOR isolated a metal oxide from the black, magnetic iron-containing sand found at Manaccan in Cornwall, and conjectured that it contained a hitherto unknown

metal, which he named manaccanite. In 1795, KLAPROTH investigated the red schorl rock from Boinik in Hungary, and he also decided that this mineral must contain an as yet unknown metal, which he named titanium after the Titans, the sons of the primeval Earth Mother. After detecting the new metal, also in oxidic form, in other minerals such as titanite and ilmenite, KLAPROTH showed that it was identical with the metal in manaccanite.

Although the fundamental reactions of modern titanium production (digestion with sulfuric acid, hydrolysis of the resulting liquor, and reduction in acidic solution) were already known before 1800, the first preparation of pure titanium oxide was carried out only in 1908, while full-scale production began in 1916 in Norway.

In 1910, HUNTER prepared 98–99% pure titanium metal by reduction with sodium. The strong affinity of titanium for oxygen, nitrogen, and carbon made preparation of the pure, ductile metal difficult, and this was first achieved by VAN ARKEL in 1922 by reducing potassium hexafluorotitanate with sodium in an inert atmosphere. The foundations for large-scale industrial production were laid by KROLL's discovery of the reduction of titanium tetrachloride by magnesium. WARTMAN of the Bureau of Mines then developed a method of treating the titanium sponge so obtained and melting it in an electric arc furnace.

22.3 Physical Properties

Pure titanium is a silvery white, ductile metal, *mp* 1668–3500 °C [15]. The atomic radius is 0.145 nm for coordination number six in the crystal lattice [16].

α -Ti has hexagonal structure of the Mg type, almost close-packed and somewhat compressed along the *c*-axis. The lattice constants of α -Ti at room temperature are *c* = 0.4679 nm, *a* = 0.2951 nm, *c/a* = 1.585 for twice-refined iodide titanium [17].

At 882.5 °C [18], titanium transforms into the body-centered cubic β -phase, the heat of transformation being 3.685 kJ/mol [19]. Ex-

trapolation of the lattice constants of titanium alloys whose β -phase can be quenched to room temperature, gives a lattice constant *a* = 0.3269 nm at room temperature [20] and 0.328 nm above 620 °C. Increasing contents of oxygen, nitrogen, and carbon, which are incorporated interstitially, slightly elongate the *a*-axis of α -Ti and considerably elongate its *c*-axis. These effects are most marked with carbon, and are very slight with hydrogen. The effect on the lattice constants of titanium of elements that form substitution mixed crystals is variable. Some important physical data of titanium are as follows:

Density at 25 °C	
high purity	4.5 g/cm ³
commercial purity	4.51
at 870 °C (α -Ti)	4.35
at 900 °C (β -Ti)	4.33
Coefficient of linear expansion at 25 °C	$8.5 \times 10^{-6} \text{ K}^{-1}$
Mean coefficient of linear expansion, 20–700 °C	$(9.0\text{--}10.1) \times 10^{-6} \text{ K}^{-1}$
Latent heat of fusion	20.9 kJ/mol
Latent heat of sublimation	464.7 kJ/mol
Latent heat of vaporization	397.8 kJ/mol
Specific heat capacity at 25 °C	0.523 J g ⁻¹ K ⁻¹
at 200 °C	0.569
at 400 °C	0.628
Thermal conductivity at 20–25 °C	
high purity	0.221 W cm ⁻¹ K ⁻¹
commercial purity	0.226–0.201
Surface tension at 1600 °C	1.7 N/m
Diffusion coefficient (self diffusion)	
at 750 °C (α -Ti)	$4 \times 10^{-13} \text{ cm}^2/\text{s}$
(β -Ti)	2.4×10^{-9}
Modulus of elasticity at 25 °C	100–110 GPa
Temperature coefficient	–0.687 GPa/K
Modulus of rigidity at 25 °C	411.8–431.5 GPa
Temperature coefficient	0.265 GPa/K
Bulk modulus at 25 °C	122.6 GPa
Transverse contraction number at 25 °C	0.30
Electrical resistivity at 25 °C	42 $\mu\Omega\text{cm}$
at 600 °C	140–150
Superconductivity (iodide titanium), transition temperature	$0.40 \pm 0.04 \text{ K}$
Magnetic susceptibility of α -Ti at 25 °C	$3.2 \times 10^{-6} \text{ cm}^3/\text{g}$
Temperature coefficient for –200 to 800 °C	$1.2 \times 10^{-9} \text{ cm}^3 \text{ g}^{-1} \text{ K}^{-1}$
Magnetic permeability at 25 °C	1.00005

Further details can be found in [13–15, 21–37]. Many properties of titanium at a given temperature show variations that depend on the composition and condition of the metal (purity, alloying elements, thermal and mechanical pretreatment).

Variation in properties such as electrical and thermal conductivity and plastic behavior are caused by lattice defects. Cold working increases hardness and strength by producing dislocations, and reduces modulus of elasticity and electrical conductivity, e.g., by producing holes in the lattice. Annealing in the recovery range (300–500 °C) and in the recrystallization range (500–800 °C) restores the original values. The moduli of elasticity and shear elasticity also depend on heat treatment. The presence of foreign elements, even at low concentrations, often has a marked effect. In general, electrical resistivity, hardness, and strength increase with decreasing purity.

22.4 Mechanical Properties

High-purity titanium (iodide and electrolytic titanium) still contains traces of other elements due to the high affinity of the metal for atmospheric gases. Above room temperature, the strength decreases, by 50% at 200 °C, whereas the fracture strain remains virtually unchanged. Increasing the grain size decreases tensile strength and yield strength but increases elongation and reduction in area at fracture. Compositions and mechanical properties of high-purity titanium grades are listed in Table 22.1.

Table 22.1: Percentage chemical compositions and strength properties of high-purity grades of titanium.

	Iodide titanium [38]	Electrolytic titanium ^a [39]
O	0.021	0.020
N	0.004	0.002
C	0.015	0.009
H		0.003
Fe	0.005	0.001
Al	0.04	
Tensile strength, MPa	230	229
Yield strength, MPa	121.5	103.0
Fracture strain ^b , %	55	55
Reduction in area, %	60	

^a Typical figures for Brinell hardness 60–65.

^b Measured length 25.4 mm (1 inch).

Titanium of Commercial Purity. As oxygen, nitrogen, and hydrogen contents increase, strength increases and toughness decreases. Whereas oxygen is the only element deliber-

ately added to give increased strength, the others, together with iron and carbon, are impurities introduced during production.

The chemical compositions and strength properties of commercial grades of titanium in the recrystallized-annealed state are listed in Table 22.2. The Grade 1 material is the softest grade of titanium, and has excellent cold working properties. It is used for deep drawing, cladding of steel reactors, as a coating applied by explosive cladding, for components that must have good corrosion resistance but need not have high strength, and in electrical technology. Titanium Grade 2 is the most widely used commercially pure titanium. It has good cold working properties, and may also be used for load-bearing components at temperatures up to ca. 250 °C. Titanium Grade 3 is used almost exclusively for pressure vessels. This material has adequate cold-working properties and can be used at lower wall thicknesses than softer grades of titanium. Titanium Grade 4 has the highest strength and is used for the manufacture of fittings and in aircraft construction. Complex components made of this grade of titanium have to be formed at ca. 300 °C.

Table 22.2: Chemical compositions (maximum contents, %) and strength properties (minimum values) of commercially pure grades of titanium.

Grade number ^a	3.7025 (Ti 1)	3.7035 (Ti 2)	3.7055 (Ti 3)	3.7065 (Ti 4)
O	0.12	0.18	0.25	0.35
N	0.05	0.05	0.05	0.05
C	0.06	0.06	0.06	0.06
H	0.013	0.013	0.013	0.013
Tensile strength, MPa	290–410	390–540	460–590	540–740
0.2% Yield strength, MPa	180	250	320	390
1% Yield strength, MPa	200	270	350	410
Fracture strain, %	24	22	18	16

^a DIN 17850, Nov. 1990, and DIN 17860, Nov. 1990.

As shown in Figure 22.1, the high-temperature tensile strength of all industrial grades of titanium decreases rapidly with increasing temperature. As titanium creeps under prolonged stress even at room temperature, the characteristic high-temperature strength val-

ues used in calculations based on 100 000 h periods, as required for chemical pressure vessels, are considerably lower than those for short periods [40]. The use of titanium Grade 1 for pressure vessels is not recommended.

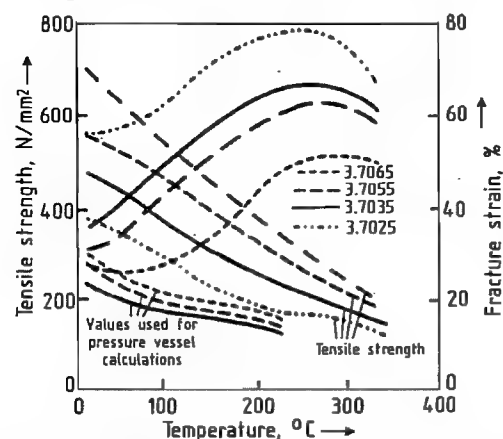


Figure 22.1: High-temperature tensile strength and fracture strain of titanium pressure vessel calculations (105 h). Titanium grade numbers are explained in Table 22.2.

In addition to the fundamental strength properties determined by destructive testing and the creep strength values determined by long-term static load tests, fatigue strength (resistance to oscillatory stress) is also important. In the case of titanium, it is between 50 and 75% of the ultimate tensile strength.

Cold working (80–90% deformation) doubles the tensile strength of titanium, and both the elongation and reduction in area at fracture decrease by ca. 50%.

22.5 Corrosion Behavior

The standard electrode potential of the reaction $\text{Ti} \rightleftharpoons \text{Ti}^{2+} + 2e^-$ is -1.75 V. The corrosion resistance of titanium metal is due to the formation of a thin, dense, stable, adherent surface film of oxide, which immediately reforms after mechanical damage if oxygen is present in the surrounding medium. Titanium is less resistant to corrosion in strongly reducing media.

The corrosion-resistant oxide layer is destroyed in completely water-free environ-

ments such as dry chlorine, dry oxygen, and red-fuming nitric acid, and in reducing corrosive media. In neutral aqueous solutions, especially in the presence of chloride ions, localized penetration of the passive layer can lead to pitting and crevice corrosion.

Passivation. In a corrosive medium, the electrode potential of a titanium surface decreases with time [41]. The passivation potential usually lies between -0.2 and -0.5 V. With increasing concentration and temperature, the passivation current density increases in the passive range, while the passivation potential remains constant [42]. The corrosion loss in the passive range therefore increases [43]. Small additions of oxidizing metal ions such as Cu^{2+} , Fe^{3+} , Cr^{4+} , Au^{3+} , and Pt^{4+} cause passivation of titanium in reducing media. With increasing temperature and acid concentration, the concentration of inhibitor necessary to give passivation increases. Anodic treatment strengthens the coatings and can delay their degradation under reducing conditions.

Additions. The corrosion behavior of titanium-based materials can often be improved by the addition of at least 0.15% palladium to the alloy, without affecting its strength properties [44, 45].

Likewise, small additions ($< 1\%$) of other noble metals improve the corrosion behavior of titanium [46]. Improvement of corrosion resistance as well as strength properties is achieved by addition of, e.g., 0.8% nickel with 0.3% molybdenum [47].

Crevice Corrosion, Stress Corrosion Cracking, and Pitting. Titanium is not very susceptible to crevice corrosion except at elevated temperatures in the presence of high concentrations of halide and sulfate ions or in moist chlorine gas. Additions of palladium to the alloy have a beneficial effect. Titanium is very resistant to pitting in the presence of chlorides, except in high concentrations of chlorides of calcium, aluminum, or zinc at elevated temperatures [48]. Titanium is not susceptible to stress corrosion cracking, except by red-fuming nitric acid containing $< 1.5\%$

water, by uranyl sulfate, or by anhydrous methanol.

Reaction with Hydrogen, Oxygen, Nitrogen, and Air. The presence of hydrogen (produced in a chemical process or as a corrosion product) or of hydrogen-containing compounds leads to local hydrogen pickup by titanium, with consequent embrittlement and impairment of corrosion resistance. The rate of hydrogen pickup depends on temperature, time, and the condition of the metal surface [49]. Oxide coatings reduce or prevent hydrogen pickup [50].

The oxide film that forms on the surface of activated titanium metal at room temperature reaches a thickness of 1.7 nm in 2 h, 3.5 nm in 40 d, and 25 nm in 4 years [51]. The color of the oxide film varies with its thickness and temperature of formation, and also with the alloy content of the parent metal. As the temperature increases from 200 to ca. 500 °C, the film thickness increases, and its color changes from golden yellow to brown, dark blue, violet, and light blue, showing iridescent effects, while at higher temperatures a gray haze forms followed by a silvery-white and then a dirty gray scale layer, after which a yellowish white to brown scale layer of variable thickness appears, depending on the alloy composition [52]. With increasing heating time and temperature, the depth of penetration of oxygen, and hence the hardness, increases [53].

Up to ca. 500 °C, the weight increase of titanium due to oxidation is small. Higher temperatures lead to a rapid weight increase associated with dissolution of oxygen in the metal.

In a nitrogen atmosphere, a titanium nitride layer with metallic character is formed. Above 700 °C, the titanium nitride increasingly reacts with oxygen to form titanium oxide. Titanium reacts with nitrogen considerably more slowly than with oxygen, so that the reaction with nitrogen makes little contribution to scale formation in air. In the presence of water vapor, hydrogen is also taken up.

Behavior in Salts, Bases, Acids, and Molten Materials. The corrosion behavior of com-

mercially pure titanium is summarized in Table 22.3. Oxidizing conditions and the presence of oxidizing agents under reducing conditions improve corrosion resistance, whereas strongly reducing conditions or increases in concentration and temperature impair it [52].

Table 22.3: Corrosion behavior of commercially pure titanium.

Resistant	Limited resistance	Nonresistant
Nitric acid	Sulfuric acid	Fluorine
Chromic acid	Hydrochloric acid	Dry chlorine gas
Sulfurous acid	Phosphoric acid	Red-fuming nitric acid
Alkali lyes	Oxalic acid	
Ammonia	Formic acid	
Aqueous chlorides		
Brine		
Seawater		
Wet chlorine gas		
Acetic acid		
Maleic acid		
Acetaldehyde		
Carbamate		
Dimethylhydrazine		
Liquid hydrogen		

Titanium is stable in molten alkali metals up to 600 °C, in magnesium up to 650 °C, in gallium, tin, lead, and lead–bismuth–tin alloys up to 300 °C, and in mercury up to 150 °C [54]. Titanium is corroded by molten mixtures of chlorides and fluorides.

22.6 Occurrence

Titanium is relatively widely distributed and abundant. With an estimated average concentration in the earth's crust of 0.6%, it is ninth in order of abundance after oxygen, silicon, aluminum, iron, magnesium, calcium, sodium, and potassium. Its concentration is ca. 1/20 that of aluminum, and 1/10 that of iron. It is 5–10 times as abundant as chlorine, sulfur, or phosphorus, and more abundant than the rest of the metals put together. Thus, for example it is 60 times as abundant as copper or nickel and 300 times as abundant as molybdenum.

As the ionic radius of titanium is similar to that of some of the most common elements (Al^{3+} , Fe^{3+} , Mg^{2+}), most minerals, rocks, and soils contain small amounts of titanium, al-

though true titanium minerals, containing > 1% titanium, of which there are at least 87, are found in only a few locations.

Primary titanium occurs in igneous rocks, where it forms the acidic component of basic magmas and the basic component of acidic magmas. In the first case, titanates are present, the most important of which are ilmenite (FeTiO_3) and perovskite (CaTiO_3). In the second case, oxidic compounds of titanium are formed. Intermediate forms also exist, e.g., in silicates, in which titanium is present mainly as a basic element (e.g., in zircon minerals and aluminosilicates), but also as a replacement for silicon. These transitional forms include titanite (sphene), $\text{CaTi}(\text{SiO}_4)\text{O}$, a common component of magmatic rocks. All these forms also occur in metamorphic titanium-containing rocks. The two TiO_2 modifications anatase and brookite occur exclusively in metamorphic deposits.

Secondary deposits of titanium include the widely distributed ilmenite placer deposits and ilmenite sands, which mostly occur in coastal regions, and the TiO_2 deposits in clays. Ilmenite is the main starting material for titanium dioxide pigments.

The most important titanium minerals are anatase (TiO_2); ilmenite (FeTiO_3), which contains up to 53% TiO_2 , and its low-iron weathering product leucoxene; perovskite (CaTiO_3); rutile (TiO_2); and sphene [$\text{CaTi}(\text{SiO}_4)\text{O}$]. Of these, only ilmenite, leucoxene, and rutile are of economic importance due to the ease with which they can be processed. The anatase deposits in Brazil and the perovskite deposits of Colorado (United States) may achieve economic importance in the future.

The most useful mineral for the extraction of titanium and titanium compounds is rutile (TiO_2). Although it is rarer than ilmenite, its TiO_2 content is higher. Naturally occurring enriched rutile is brown to black, and contains 90–97% TiO_2 together with impurities including up to 10% silica, iron oxides, vanadium, niobium, and tantalum, and traces of tin, chromium, and molybdenum compounds.

Primary rutile deposits occur at Kragero in south east Norway (albite with 25% rutile)

and in Virginia (United States). However, more important are the secondary placer deposits, e.g., in Brazil, Cameroon, and Arkansas (United States), and the beach sands, of which the most important are on the east coasts of Australia and Florida (United States) and in northern Transvaal (South Africa). All rutile and two-thirds of ilmenite are extracted from placer deposits and sands, the rest of the ilmenite being obtained from titanomagnetites and titanohematites.

Rutile-bearing beach and dune deposits can be mined if TiO_2 contents exceed 0.3%. The TiO_2 content of the ilmenite sands depends on the degree of weathering. In the South African deposits it is 10–48%, in Australian sands 54%, and in ilmenite from Kerala (India) and the east coast of Sri Lanka up to 80%. The ilmenite-bearing titanomagnetites and titanohematites contain 35% TiO_2 in Canada, ca. 20% in the United States, 18% in Norway, and 13% in Finland [55].

Titanium occurs in many stars. It is less abundant in meteorites than in the earth's crust, and is mainly associated with the silicate phase [56].

Reserves. Proven world reserves of rutile and ilmenite, calculated as TiO_2 , content have been estimated at 423×10^6 to 600×10^6 t. The largest reserves of ilmenite are in South Africa, India, the United States, Canada, Norway, Australia, Ukraine, Russia, and Kazakhstan, and of rutile in Brazil [57]. The existence of other reserves, e.g., in Bangladesh, Chile, Italy, Mexico, and New Zealand, makes it likely that the actual mineable world reserves considerably exceed the accepted figures.

22.7 Titanium Dioxide

Titanium dioxide, TiO_2 , occurs in nature in the modifications rutile, anatase, and brookite. Rutile and anatase are produced industrially in large quantities and are used as pigments and catalysts, and in the production of ceramic materials.

Titanium dioxide is of outstanding importance as a white pigment because of its scattering properties (which are superior to those of all other white pigments), its chemical stability, and lack of toxicity. Titanium dioxide is the most important inorganic pigment in terms of quantity, 3×10^6 t were produced in 1989. World production of titanium dioxide pigment is shown in Table 22.4 [58].

Table 22.4: World production of TiO_2 pigment.

Year	Sulfate process		Chloride process		Total 10^3 t/a
	10^3 t/a	%	10^3 t/a	%	
1965	1254	90.3	135	9.7	1389
1970	1499	77.4	437	22.6	1936
1977	1873	72.3	716	27.7	2589
1988	1781	60.2	1178	39.8	2959
1995*	2000	ca. 49	2100	51.0	4100

*Estimated.

22.7.1 Properties [59, 60]

Physical Properties. Of the three modifications of TiO_2 , rutile is the most thermodynamically stable. Nevertheless, the lattice energies of the other phases are similar and hence are stable over long periods. Above 700 °C, the monotropic conversion of anatase to rutile takes place rapidly. Brookite is difficult to produce, and therefore has no value in the TiO_2 pigment industry.

In all three TiO_2 modifications one titanium atom in the lattice is surrounded octahedrally by six oxygen atoms, and each oxygen atom is surrounded by three titanium atoms in a trigonal arrangement. The three modifications correspond to different ways of linking the octahedra at their corners and edges. Crystal lattice constants and densities are given in Table 22.5.

Table 22.5: Crystallographic data for TiO_2 modifications.

Phase	Crystal system	Lattice constants, nm			Density, g/cm^3
		a	b	c	
Rutile	tetragonal	0.4594		0.2958	4.21
Anatase	tetragonal	0.3785		0.9514	4.06
Brookite	rhombic	0.9184	0.5447	0.5145	4.13

Rutile and anatase crystallize in the tetragonal system, brookite in the rhombic system. The melting point of TiO_2 is ca. 1800 °C.

Above 1000 °C, the oxygen partial pressure increases continuously as oxygen is liberated and lower oxides of titanium are formed. This is accompanied by changes in color and electrical conductivity. Above 400 °C, a significant yellow color develops, caused by thermal expansion of the lattice; this is reversible. Rutile has the highest density and the most compact atomic structure, and is thus the hardest modification (Mohs hardness 6.5–7.0). Anatase is considerably softer (Mohs hardness 5.5).

Titanium dioxide is a light-sensitive semiconductor, and absorbs electromagnetic radiation in the near UV region. The energy difference between the valence and the conductivity bands in the solid state is 3.05 eV for rutile and 3.29 eV for anatase, corresponding to an absorption band at < 415 nm for rutile and < 385 nm for anatase.

Absorption of light energy causes an electron to be excited from the valence band to the conductivity band. This electron and the electron hole are mobile, and can move on the surface of the solid where they take part in redox reactions.

Chemical Properties. Titanium dioxide is amphoteric with very weak acidic and basic character. Accordingly, alkali-metal titanates and free titanate acids are unstable in water, forming amorphous titanium oxide hydroxides on hydrolysis.

Titanium dioxide is chemically very stable, and is not attacked by most organic and inorganic reagents. It dissolves in concentrated sulfuric acid and in hydrofluoric acid, and is attacked and dissolved by alkaline and acidic molten materials.

At high temperature, TiO_2 reacts with reducing agents such as carbon monoxide, hydrogen, and ammonia to form titanium oxides of lower valency; metallic titanium is not formed. Titanium dioxide reacts with chlorine in the presence of carbon above 500 °C to form titanium tetrachloride.

Surface Properties of TiO_2 Pigments. The specific surface area of TiO_2 pigments can vary between 0.5 and 300 m^2/g depending on

its use. The surface of TiO_2 is saturated by coordinatively bonded water, which then forms hydroxyl ions. Depending on the type of bonding of the hydroxyl groups to the titanium, these groups possess acidic or basic character [61, 62]. The surface of TiO_2 is thus always polar. The surface covering of hydroxyl groups has a decisive influence on pigment properties such as dispersibility and weather resistance.

The presence of the hydroxyl groups makes photochemically induced reactions possible, e.g., the decomposition of water into hydrogen and oxygen and the reduction of nitrogen to ammonia and hydrazine [63].

22.7.2 Raw Materials [64]

The raw materials for TiO_2 production include natural products such as ilmenite, leucoxene, and rutile, and some very important synthetic materials such as titanium slag and synthetic rutile. Production capacities for the most important titanium-containing raw materials are listed in Table 22.6 [65].

Table 22.6: Production capacities of titanium-containing raw materials (1987).

Raw material	Location	Capacity, 10^3 t/a
Ilmenite	Australia	1550
	India	240
	Malaysia	130
	Sri Lanka	150
	Brazil	80
	United States	260
	Norway	650
	Total	3060
Natural rutile	Australia	250
	Sierra Leone	125
	South Africa	55
	United States	27
	Others	33
	Total	490
Titanium slag	Canada	1000
	South Africa	650
	Norway	200
	Total	1850
Synthetic rutile	Australia	272
	India	50
	Japan	48
	United States	100
	Total	470

22.7.2.1 Natural Raw Materials

Titanium is the ninth most abundant element in the earth's crust, and always occurs in combination with oxygen. The more important titanium minerals are shown in Table 22.7. Of the natural titanium minerals, only ilmenite (leucoxene) and rutile are of economic importance. Leucoxene is a weathering product of ilmenite.

Table 22.7: Titanium minerals.

Mineral	Formula	TiO_2 , %
Rutile	TiO_2	92–98
Anatase	TiO_2	90–95
Brookite	TiO_2	90–100
Ilmenite	FeTiO_3	35–60
Leucoxene	$\text{Fe}_2\text{O}_3\cdot\text{TiO}_2$	60–90
Perovskite	CaTiO_3	40–60
Sphene (titanite)	CaTiSiO_5	30–42
Titanomagnetite	$\text{Fe}(\text{Ti})\text{Fe}_2\text{O}_4$	2–20

The largest titanium reserves in the world are in the form of anatase and titanomagnetite, but these cannot be worked economically at the present time. About 95% of the world's production of ilmenite and rutile is used to produce TiO_2 pigments, the remainder for the manufacture of titanium metal and in welding electrodes.

Ilmenite and Leucoxene. Ilmenite is found worldwide in primary massive ore deposits or as secondary alluvial deposits (sands) that contain heavy minerals. In the massive ores, the ilmenite is frequently associated with intermediary intrusions (Tellnes in Norway and Lake Allard in Canada). The concentrates obtained from these massive ores often have high iron contents in the form of segregated hematite or magnetite in the ilmenite. These reduce the TiO_2 content of the concentrates (Table 22.8). Direct use of these ilmenites has decreased owing to their high iron content. A digestion process is employed to produce iron sulfate heptahydrate. In cases where iron sulfate is not required as a product, metallurgical recovery of iron from the iron-rich ilmenites and production of a titanium-rich slag are being increasingly used.

The enrichment of ilmenite in beach sand in existing or fossil coastlines is important for

TiO_2 production. The action of surf, currents, and/or wind results in concentration of the ilmenite and other heavy minerals such as rutile, zircon, monazite, and other silicates in the dunes or beaches. This concentration process frequently leads to layering of the minerals. Attack by seawater and air over geological periods of time leads to corrosion of the ilmenite. Iron is removed from the ilmenite lattice, resulting in enrichment of the TiO_2 in the remaining material. The lattice is stable with TiO_2 contents up to ca. 65%, but further removal of iron leads to the formation of a sub-microscopic mixture of minerals which may include anatase, rutile, and amorphous phases. Mixtures with TiO_2 contents as high as 90% are referred to as leucoxene. Leucoxene is present in corroded ilmenite and in some deposits is recovered and treated separately. However, the quantities produced are small in comparison to those of ilmenite.

The concentrates obtained from ilmenite sand, being depleted in iron, are generally richer in TiO_2 than those from the massive deposits. Other elements in these concentrates include magnesium, manganese, and vanadium (present in the ilmenite) and aluminum, calcium, chromium, and silicon which originate from mineral intrusions.

Table 22.8: Composition of ilmenite deposits (%).

Component	Tellnes (Norway)	Richard's Bay (South Africa)	Capel (Western Australia)	Quilon (India)
TiO_2	43.8	46.5	54.8	60.3
Fe_2O_3	14.0	11.4	16.0	24.8
FeO	34.4	34.2	23.8	9.7
Al_2O_3	0.6	1.3	1.0	1.0
SiO_2	2.2	1.6	0.8	1.4
MnO	0.3		1.5	0.4
Cr_2O_3		0.1	0.1	0.1
V_2O_5	0.3	0.3	0.2	0.2
MgO	3.7	0.9	0.15	0.9

Two-thirds of the known ilmenite reserves that could be economically worked are in China, Norway (both massive deposits), and the former Soviet Union (sands and massive deposits). On the basis of current production capacities, these countries could cover all requirements for ca. 150 years. However, the countries with the largest outputs are Australia

(sands), Canada (massive ore), South Africa (sands), and the former Soviet Union (sands, massive ore). Other producers are the United States (sands, Florida), India (sands, Quilon), Sri Lanka (sands), and Brazil (rutile e ilmenita do Brasil). Important deposits have been found in Madagascar.

Rutile is formed primarily by the crystallization of magma with high titanium and low iron contents, or by the metamorphosis of titanium-bearing sediments or magmatites. The rutile concentrations in primary rocks are not workable. Therefore, only sands in which rutile is accompanied by zircon and/or ilmenite and other heavy minerals can be regarded as reserves. The world reserves of rutile are estimated to be 28×10^6 t, including the massive Piampaludo ore reserves in Italy, whose workability is in dispute.

As in the case of ilmenite, the largest producers are in Australia, South Africa, the United States, and India. There is not enough natural rutile to meet demand, and it is therefore gradually being replaced by the synthetic variety. Compositions of typical rutile concentrates are given in Table 22.9.

Table 22.9: Composition of rutile deposits [66].

Rutile component	Content, %		
	Eastern Australia	Sierra Leone	South Africa
TiO_2	96.00	95.70	95.40
Fe_2O_3	0.70	0.90	0.70
Cr_2O_3	0.27	0.23	0.10
MnO	0.02		
Nb_2O_5	0.45	0.21	0.32
V_2O_5	0.50	1.00	0.65
ZrO_2	0.50	0.67	0.46
Al_2O_3	0.15	0.20	0.65
CaO	0.02		0.05
P_2O_5	0.02	0.04	0.02
SiO_2	1.00	0.70	1.75

Anatase, like rutile, is a modification of TiO_2 . The largest reserves of this mineral are found in carboniferous intrusions in Brazil. Ore preparation techniques allow production of concentrates containing 80% TiO_2 , with possible further concentration to 90% TiO_2 by treatment with hydrochloric acid [67]. Attempts to use these substantial mineral depos-

its ($< 100 \times 10^6$ t TiO_2) as a pigment raw material are at the pilot-plant stage.

Ore Preparation. Most of the world's titanium ore production starts from heavy mineral sands. Figure 22.2 shows a schematic of the production process. The ilmenite is usually associated with rutile and zircon, so that ilmenite production is linked to the recovery of these minerals. Geological and hydrological conditions permitting, the raw sand (usually containing 3–10% heavy minerals) is obtained by wet dredging (a). After a sieve test (b), the raw sand is subjected to gravity concentration in several stages with Reichert cones (d) and/or spirals (e) to give a product containing 90–98% heavy minerals. This equipment separates the heavy from the light minerals (densities: 4.2–4.8 g/cm³ and < 3 g/cm³ respectively) [68].

The magnetic minerals (ilmenite) are then separated from the nonmagnetic (rutile, zircon, and silicates) by dry or wet magnetic separation (f). If the ores are from unweathered deposits, the magnetite must first be removed. An electrostatic separation stage (h) allows separation of harmful nonconducting mineral impurities such as granite, silicates, and phosphates from the ilmenite, which is a good conductor. The nonmagnetic fraction (leucosene, rutile, and zircon) then undergoes further hydromechanical processing (i) (shaking table, spirals) to remove the remaining low-density minerals (mostly quartz). Recovery of the weakly magnetic weathered ilmenites and leucosenes is by high-intensity magnetic separation (j) in a final dry stage. The conducting rutile is then separated from the nonconducting zircon electrostatically in several stages (l). Residual quartz is removed by an air blast.

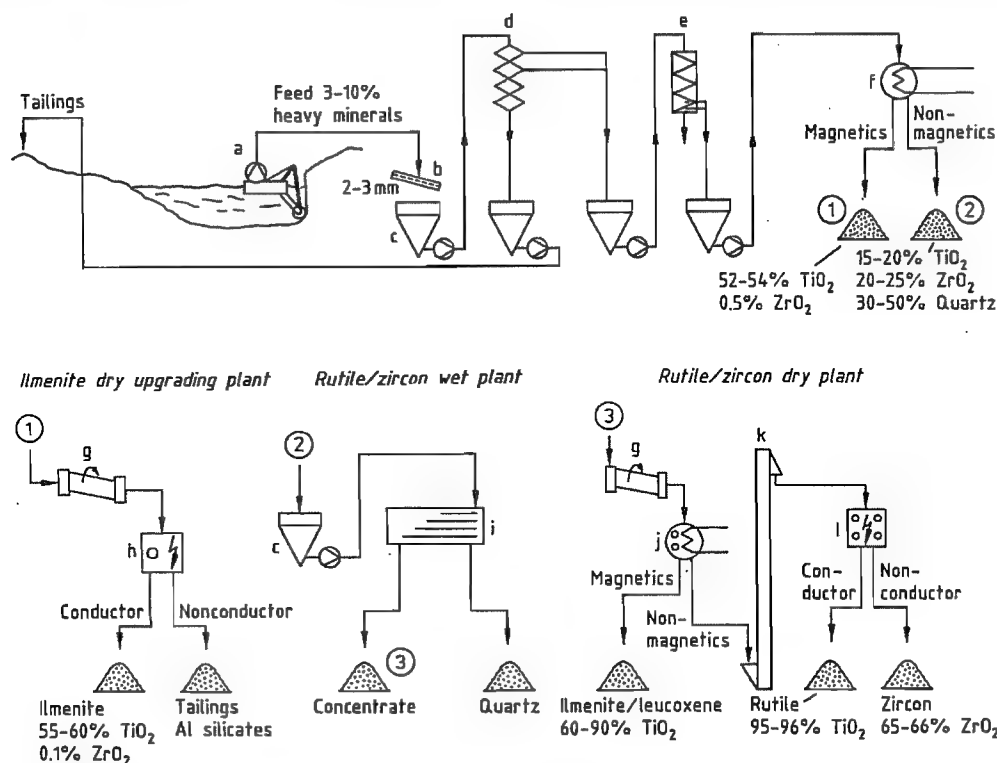


Figure 22.2: The processing of heavy mineral sands: a) Dredger; b) Sieve; c) Bunker; d) Reichert cones; e) Spirals; f) Magnetic separator; g) Dryer; h) Electrostatic separator; i) Shaking table; j) Dry magnetic separator; k) Vertical belt conveyor; l) Electrostatic separator.

Table 22.10: Production plants for synthetic rutiles in 1987 [80].

Process development	Process steps	By-products	Producer and location ^a
Benilite Corporation of America (BCA)	partial reduction to Fe(II), digestion with HCl solution, calcination	20–23% FeCl_2 , pyrolyzed to Fe_2O_3 and HCl	Kerr McGee, Mobile, USA (100); Kerala Minerals and Metals Ltd., Chavara, Kerala (25); Indian Rare Earths, Orissa, India (100)
Western Titanium	oxidation to Fe(III), reduction to Fe(0), digestion with FeCl_2 , with air oxidation	iron hydroxides	Associated Minerals Consolidated, Casl, Australia (60); AMC, Narmgulu, Australia (112)
Lurgi	reduction to Fe(0), digestion with air blowing, hydrocyclone separation, calcination	iron hydroxides	Westralian Sand Ltd., Capel, Australia (100)
Ishibara Sangyo Kaisha	reduction to Fe(II), digestion with H_2SO_4 , calcination	FeSO_4 solution reacted with NH_3 to form ammonium sulfate and iron hydroxide	Ishibara, Yokkaichi, Japan (48)
Dhrangadhra Chemical Works	reduction to Fe(II)/Fe(0), digestion with HCl solution, calcination	iron(II) chloride solution	Dhrangadhra Chemical Works Ltd., Suhupuram, Tamil Nadu, India (25)

^aCapacity in 10^3 t is given in parentheses.

22.7.2.2 Synthetic Raw Materials

Increasing demand for raw materials with high TiO_2 contents has led to the development of synthetic TiO_2 raw materials. In all production processes, iron is removed from ilmenites or titanomagnetites.

Titanium Slag. The metallurgical process for removing iron from ilmenite is based on slag formation in which the iron is reduced by anthracite or coke to metal at 1200–1600 °C in an electric arc furnace, and then separated. Titanium-free pig iron is produced together with slags containing 70–85% TiO_2 (depending on the ore used) that can be digested with sulfuric acid because they are high in Ti^{3+} and low in carbon. Raw materials of this type are produced in Canada by the Québec Iron and Titanium Corporation (QIT), in South Africa by Richard's Bay Iron and Titanium Ltd. (RBM), and to a smaller extent in Japan by Hokueto Metal and Tinfos Titan and Iron K.S. (Tyssedal, Norway).

Synthetic Rutile. In contrast to ilmenite, only a small number of rutile deposits can be mined economically, and the price of natural rutile is therefore high. Consequently, many different processes have been developed to remove the iron from ilmenite concentrates without changing the grain size of the mineral because

this is highly suitable for the subsequent fluidized-bed chlorination process. All industrial processes involve reduction of Fe^{3+} with carbon or hydrogen, sometimes after preliminary activation of the ilmenite by oxidation. Depending on the reducing conditions, either Fe^{2+} is formed in an activated ilmenite lattice, or metallic iron is produced.

The activated Fe^{2+} -containing ilmenite can be treated with hydrochloric or dilute sulfuric acid (preferably under pressure), and a "synthetic rutile" with a TiO_2 content of 85–96% is obtained [69]. The solutions containing iron(II) salts are concentrated and then thermally decomposed to form iron oxide and the free acid, which can be used again in the digestion process [70].

Metallic iron can be removed in various ways. The following processes are described in the patent literature:

- Size reduction followed by physical processes such as magnetic separation of flotation.
- Dissolution in iron(III) chloride solutions [71], the resulting iron(II) salt is oxidized with air to give iron oxide hydroxides and iron(III) salts.
- Dissolution in acid.

- Oxidation with air in the presence of electrolytes. Various iron oxide or iron oxide hydroxide phases are formed depending on the electrolyte used. Possible electrolytes include iron(II) chloride solutions [72], ammonium chloride [73], or ammonium carbonate carbonic acid [74].
- Oxidation with the iron(III) sulfate from ilmenite digestion [75], followed by crystallization of the iron(II) sulfate.
- Chlorination to form iron(III) chloride [76].
- Reaction with carbon monoxide to form iron carbonyls [77] which can be decomposed to give high-purity iron.

Another possible method of increasing the TiO_2 content of ilmenite is by partial chlorination of the iron in the presence of carbon. This is operated on a large scale by several compa-

nies [78, 79]. Table 22.10 summarizes plants producing synthetic rutile in 1987.

22.7.3 Production

Titanium dioxide pigments are produced by two different processes. The older *sulfate process* depends on the breakdown of the titanium-containing raw material ilmenite or titanium slag with concentrated sulfuric acid at 150–220 °C. Relatively pure TiO_2 dihydrate is precipitated by hydrolysis of the sulfate solution, which contains colored heavy metal sulfates, sometimes in high concentration. The impurities are largely removed in further purification stages. The hydrate is then calcined, ground, and further treated.

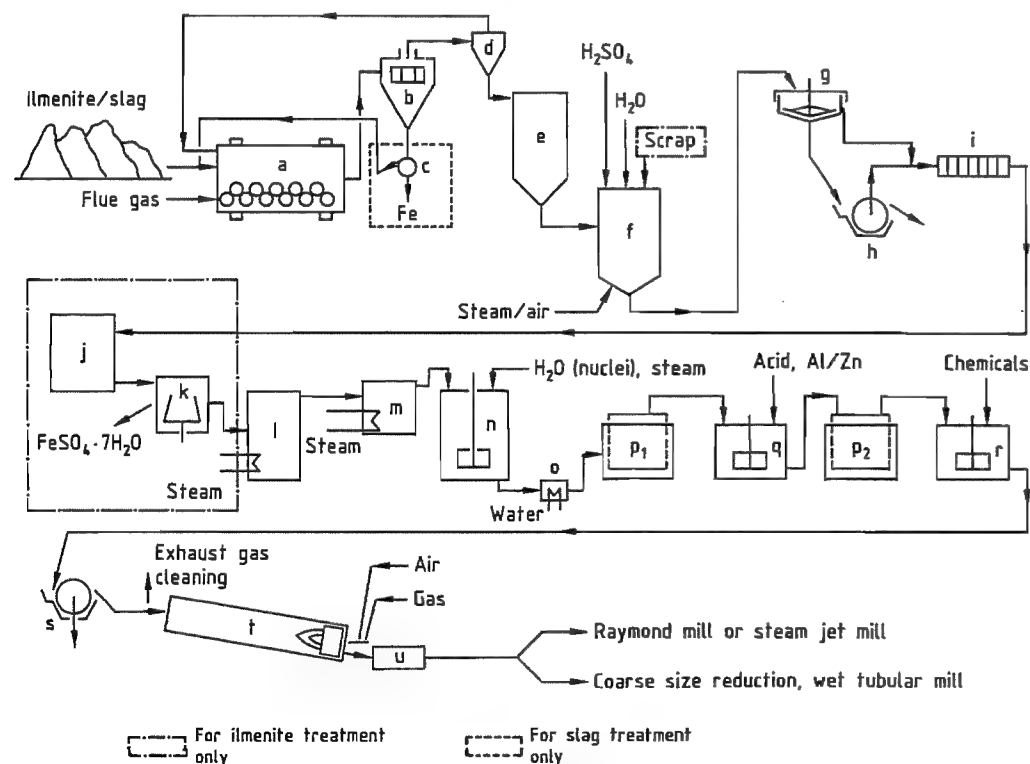


Figure 22.3: Production of TiO_2 by the sulfate process: a) Ball mill/dryer; b) Screen; c) Magnetic separator; d) Cyclone; e) Silo; f) Digestion vessel; g) Thickener; h) Rotary filter; i) Filter press; j) Crystallizer; k) Centrifuge; l) Vacuum evaporator; m) Preheater; n) Stirred tank for hydrolysis; o) Cooler; p) Moore filters; q) Stirred tank for bleaching; r) Stirred tank for doping; s) Rotary filter for dewatering; t) Rotary kiln; u) Cooler.

In the *chloride process*, the titanium-containing raw materials ilmenite, leucoxene, natural and synthetic rutile, titanium slag, and anatase are chlorinated at 700–1200 °C. Titanium tetrachloride is separated from other chlorides by distillation. Vanadium tetrachloride (VCl_4) and vanadium oxychloride (VOCl_3) must, however, first be reduced to solid chlorides. The TiCl_4 is burnt at temperatures of 900–1400 °C to form TiO_2 . This extremely pure pigment undergoes further treatment depending on the type of application.

22.7.3.1 Sulfate Method

The sulfate method is summarized in Figure 22.3.

Grinding. The titanium-bearing raw materials are dried to a moisture content of < 0.1%. Drying is mainly intended to prevent heating and premature reaction on mixing with sulfuric acid. The raw materials are ground in ball mills to give a mean particle size of ca. 40 μm . The combination of grinding and drying shown in Figure 22.3 (a) is recommended. The small amount of metallic iron present in titanium slag is removed magnetically (c), which almost completely eliminates hydrogen evolution during subsequent digestion.

Digestion. Batch digestion is usually employed. The ground raw materials (ilmenite, titanium slag, or mixtures of the two) are mixed with 80–98% H_2SO_4 . The ratio of H_2SO_4 to raw material is chosen so that the weight ratio of free H_2SO_4 to TiO_2 in the suspension produced by the hydrolysis is between 1.8 and 2.2 (the so-called “acid number”). The reaction in the digestion vessel (f) is started by adding water, dilute sulfuric acid, oleum, or sometimes steam. The temperature initially increases to 50–70 °C due to the heat of hydration of the acid. The exothermic sulfate formation then increases the temperature to 170–220 °C. If dilute acid or sparingly soluble raw materials are used, external heating is required.

After the maximum temperature has been reached, the reaction mixture must be left to mature for 1–12 h, depending on the raw material, so that the titanium-containing components become as soluble as possible. Digestion can be accelerated by blowing air through the mass while the temperature is increasing, and also during the maturing period.

Several *continuous digestion processes* have been proposed [81]. A proven method is to continuously feed a mixture of ilmenite and water together with the acid into a double-paddle screw conveyor. After a relatively short dwell time (< 1 h), a crumbly cake is produced [82]. This process utilizes a more limited range of raw materials than the batch process because they need to be very reactive.

Dissolution and Reduction. The cake obtained by digestion is dissolved in cold water or in dilute acid recycled from the process. A low temperature must be maintained (< 85 °C) to avoid premature hydrolysis, especially with the product from ilmenite. Air is blown in to agitate the mixture during dissolution. With the ilmenite product, the TiO_2 concentration of the solution is 8–12%, and with the slag product between 13 and 18%.

The trivalent iron is hydrolyzed together with the titanium compounds, and adheres to the titanium oxide hydrate. All the Fe^{3+} is reduced to Fe^{2+} by scrap iron during dissolution of the ilmenite product, or immediately afterwards. Reoxidation of the iron during subsequent processing is prevented with Ti^{3+} which is obtained by reducing a small part of the Ti^{4+} . Alternatively, reduction of Ti^{4+} to Ti^{3+} can be carried out in part of the solution under optimized conditions; this concentrated Ti^{3+} solution is then added in a controlled manner to the reaction solution [83]. In solutions obtained from titanium slag, the Ti^{3+} content of the solution must be decreased by oxidation with atmospheric oxygen so that no loss of yield occurs during hydrolysis.

With both ilmenite and titanium slag, mixed digestion can be carried out in which the Ti^{3+} content of the slag reduces all the Fe^{3+} to Fe^{2+} . The dissolved products obtained from

the separate digestion of ilmenite and titanium slag can also be mixed [84, 85].

Clarification. All undissolved solid material must be removed as completely as possible from the solution. The most economical method is to employ preliminary settling in a thickener (g), followed by filtration of the sediment with a rotary vacuum filter (h). The filtrate and the supernatant from the thickener are passed through filter presses (i) to remove fines. Owing to the poor filtering properties of the solution, the rotary filter must be operated as a precoat filter. Preliminary separation in the thickener must be assisted by adding chemicals to promote sedimentation. Attempts to carry out the entire clarification process in a single stage using automated filter presses have been reported [86].

Crystallization. The solutions from slag digestion contain 5–6% FeSO_4 , and those from ilmenite digestion 16–20% FeSO_4 after reduction of the Fe^{3+} . The solution is cooled under vacuum to crystallize out $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (j) and reduce the quantity of FeSO_4 discharged with the waste acid. The concentration of the TiO_2 in the solution is thereby increased by ca. 25%. The salt is separated by filtration or centrifugation (k).

The iron sulfate is used in water purification, and as a raw material for the production of iron oxide pigments. Alternatively, it can be dehydrated and thermally decomposed to give iron(III) oxide and sulfur dioxide.

Hydrolysis. Titanium oxide hydrate is precipitated by hydrolysis at 94–110 °C. Other sulfuric-acid-soluble components of the raw material are precipitated simultaneously, mainly niobium as its oxide hydrate.

Hydrolysis is carried out in brick-lined, stirred tanks (n) into which steam is passed. The hydrolysate does not have any pigment properties, but these are strongly influenced by the particle size and degree of flocculation of the hydrolysate (mean particle size of hydrolysate is ca. 5 nm, and of TiO_2 pigments 200–300 nm).

The properties of the hydrolysate depend on several factors:

- The hydrolysis of concentrated solutions of titanium sulfate (170–230 g TiO_2/L) proceeds very sluggishly and incompletely (even if boiled) unless suitable nuclei are added or formed to accelerate hydrolysis. The nuclei are usually produced by two methods. In the Mecklenburg method, colloidal titanium oxide hydrate is precipitated with sodium hydroxide at 100 °C; 1% of this hydrate is sufficient. In the Blumenfeld method a small part of the sulfate solution is hydrolyzed in boiling water and then added to the bulk solution [87]. The particle size of the hydrolysate depends on the number of nuclei.
- The particle size and degree of flocculation of the hydrolysate depend on the intensity of agitation during the nuclei formation by the Blumenfeld method and also during the initial stage of the hydrolysis.
- The titanium sulfate concentration has a great influence on the flocculation of the hydrolysate. It is adjusted, if necessary by vacuum evaporation, to give a TiO_2 content of 170–230 g/L during hydrolysis. Lower concentrations result in a coarser particle size.
- The acid number should be between 1.8 and 2.2. It has a considerable effect on the TiO_2 yield and on the particle size of the hydrolysate. For a normal hydrolysis period (3–6 h) the TiO_2 yield is 93–96%.
- The properties of the hydrolysate are affected by the concentrations of other salts present, especially FeSO_4 . High concentrations lead to finely divided hydrolysates.
- The temperature regime mainly affects the volume–time yield and hence the purity of the hydrolysate.

Purification of the Hydrolysate. After hydrolysis, the liquid phase of the titanium oxide hydrate suspension contains 20–28% H_2SO_4 and various amounts of dissolved sulfates, depending on the raw material. The hydrate is filtered off from the solution (p_1) (weak acid), and washed with water or dilute acid. Even

with acid washing, too many heavy metal ions are adsorbed on the hydrate for it to be directly usable in the production of white pigment. Most of the impurities can be removed by reduction (bleaching), whereby the filter cake is slurried with dilute acid (3–10%) at 50–90 °C and mixed with zinc or aluminum powder (q). Bleaching can also be carried out with powerful nonmetallic reducing agents (e.g., $\text{HOCH}_2\text{SO}_2\text{Na}$). After a second filtration and washing process (p_2), the hydrate only has low concentrations (ppm) of colored impurities but still contains chemisorbed 5–10% H_2SO_4 . This cannot be removed by washing and is driven off by heating to a high temperature.

Doping of the Hydrate. When producing titanium dioxide of maximum purity, the hydrate is heated (calcined) without any further additions. This gives a fairly coarse grade of TiO_2 with a rutile content that depends on the heating temperature. However, to produce specific pigment grades, the hydrate must be treated with alkali-metal compounds and phosphoric acid as mineralizers (< 1%) prior to calcination (r). Anatase pigments contain more phosphoric acid than rutile pigments. To produce rutile pigments, rutile nuclei (< 10%) must be added; ZnO , Al_2O_3 , and/or Sb_2O_3 (< 3%) are sometimes also added to stabilize the crystal structure.

Nuclei are produced by converting the purified titanium oxide hydrate to sodium titanate, which is washed free of sulfate and then treated with hydrochloric acid to produce the rutile nuclei. Rutile nuclei can also be prepared by precipitation from titanium tetrachloride solutions with sodium hydroxide solution.

Calcination. The doped hydrate is filtered with rotary vacuum filters (s) to remove water until a TiO_2 content of ca. 30–40% is reached. Pressure rotary filters or automatic filter presses can also be used to obtain a TiO_2 content of ca. 50%. Some of the water-soluble dopants are lost in the filtrate and can be replaced by adding them to the filter cake before it is charged into the kiln. Calcination is performed in rotary kilns (t) directly heated with gas or oil in countercurrent flow. Approxi-

mately two-thirds of the residence time (7–20 h in total) is needed to dry the material. Above ca. 500 °C, sulfur trioxide is driven off which partially decomposes to sulfur dioxide and oxygen at higher temperatures. The product reaches a maximum temperature of 800–1100 °C depending on pigment type, throughput, and temperature profile of the kiln. Rutile content, particle size, size distribution, and aggregate formation are extremely dependent on the operating regime of the kiln. After leaving the kiln, the clinker can be indirectly cooled or directly air-cooled in drum coolers (u).

The exhaust gas must have a temperature of > 300 °C at the exit of the kiln to prevent condensation of sulfuric acid in the ducting. Energy can be saved by recirculating some of the gas to the combustion chamber of the kiln and mixing it with the fuel gases as a partial replacement for air. Alternatively, it can be used for concentrating the dilute acid. The gas then goes to the waste-gas purification system.

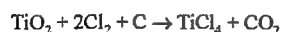
Grinding. The agglomerates and aggregates in the clinker can be reduced to pigment fineness by wet or dry grinding. Coarse size reduction should be carried out in hammer mills prior to wet grinding in tube mills (with addition of wetting agents). The coarse fraction can be removed from the suspension by centrifugation, and recycled to the mills. Hammer mills, cross-beater mills, and particularly pendular and steam-jet mills are suitable for dry grinding. Special grinding additives can be used that act as wetting agents during subsequent pigment treatment or improve the dispersibility of untreated pigments.

22.7.3.2 The Chloride Process

The chloride process is summarized in Figure 22.4.

Chlorination. The titanium in the raw material is converted to titanium tetrachloride in a reducing atmosphere. Calcined petroleum coke is used as the reducing agent because it has an extremely low ash content and, due to its low volatiles content, very little HCl is

formed. The titanium dioxide reacts exothermically as follows:



As the temperature rises, an endothermic reaction also occurs to an increasing extent in which carbon monoxide is formed from the carbon dioxide and carbon. Therefore, oxygen must be blown in with the chlorine to maintain the reaction temperature between 800 and 1200 °C. The coke consumption per tonne of TiO_2 is 250–300 kg. If CO_2 -containing chlorine from the combustion of TiCl_4 is used, the coke consumption increases to 350–450 kg.

The older *fixed-bed chlorination method* is hardly used today. In this process, the ground titanium-containing raw material is mixed with petroleum coke and a binder, and formed into briquettes. Chlorination is carried out at 700–900 °C in brick-lined reactors.

Fluidized-bed chlorination was started in 1950. The titanium raw material (with a particle size similar to that of sand) and petroleum coke (with a mean particle size ca. five times that of the TiO_2) are reacted with chlorine and oxygen in a brick-lined fluidized-bed reactor (Figure 22.4, c) at 800–1200 °C. The raw materials must be as dry as possible to avoid HCl formation. Since the only losses are those due to dust entrainment the chlorine is 98–100% reacted, and the titanium in the raw material is 95–100% reacted, depending on the reactor design and the gas velocity. Magnesium chloride and calcium chloride can accumulate in the fluidized-bed reactor due to their low volatility. Zirconium silicate also accumulates because it is chlorinated only very slowly at the temperatures used. All the other constituents of the raw materials are volatilized as chlorides in the reaction gases.

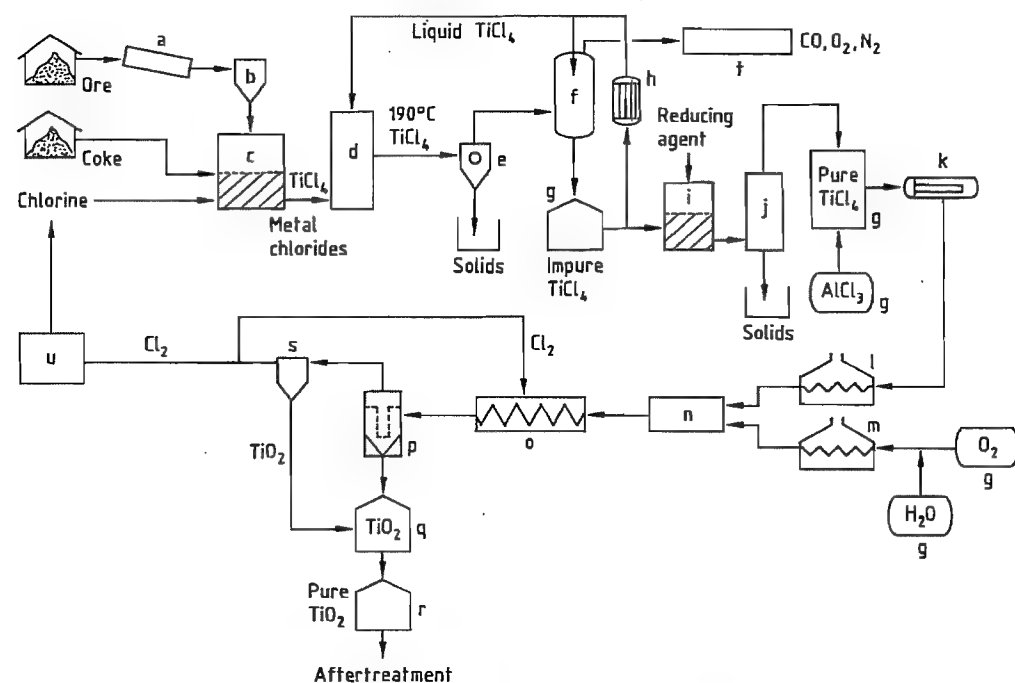


Figure 22.4: Flow diagram of TiO_2 production by the chloride process: a) Mill; b) Silo; c) Fluidized-bed reactor; d) Cooling tower; e) Separation of metal chlorides; f) TiCl_4 condensation; g) Tank; h) Cooler; i) Vanadium reduction; j) Distillation; k) Evaporator; l) TiCl_4 superheater; m) O_2 superheater; n) Burner; o) Cooling coil; p) Filter; q) TiO_2 purification; r) Silo; s) Gas purification; t) Waste-gas cleaning; u) Cl_2 liquefaction.

The ceramic cladding of the fluidized-bed reactor is rather rapidly destroyed by abrasion and corrosion. If chlorination is interrupted, there is a further danger that the raw materials may sinter and eventually cannot be fluidized.

Gas Cooling. The reaction gases are cooled with liquid TiCl_4 either indirectly or directly (d). Crystallization of the chlorides of the other components causes problems because they tend to build up on the cooling surfaces, especially the large quantities of iron(II) and iron(III) chlorides formed on chlorination of ilmenite [88]. In this first stage, the reaction gases are cooled only down to a temperature (< 300 °C) at which the accompanying chlorides can be satisfactorily separated from the TiCl_4 by condensation or sublimation (e).

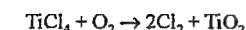
The gas then consists mainly of TiCl_4 and is cooled below 0 °C, causing most of the TiCl_4 to condense (f). The small amounts of TiCl_4 and Cl_2 remaining in the exhaust gas (CO_2 , CO , and N_2) are removed by scrubbing with alkali (t).

Purification of TiCl_4 . The chlorides that are solid at room temperature and the entrained dust can be separated from the TiCl_4 by simply evaporating (distilling) this off (j). Dissolved chlorine can be removed by heating or reduction with metal powders (Fe, Cu, or Sn).

Removal of vanadium tetrachloride (VCl_4) and vanadium oxychloride (VOCl_3) from the TiCl_4 by distillation is very difficult owing to the closeness of their boiling points. They are therefore reduced to form solid, low-value vanadium chlorides (i). An enormous number of reducing agents have been recommended; important examples are copper, titanium trichloride, hydrogen sulfide, hydrocarbons, soaps, fatty acids, and amines. After subsequent evaporation (j) the titanium chloride should contain < 5 ppm vanadium. If organic reducing agents are used, the residues may cause problems by baking onto the surfaces of the heat exchanger.

Phosgene and SiCl_4 can be removed by fractional distillation.

Oxidation of TiCl_4 and Recovery of TiO_2 . Titanium tetrachloride is combusted with oxygen at 900–1400 °C to form TiO_2 pigment and chlorine (n). The purified TiCl_4 is vaporized (k) and the vapor is indirectly heated to ca. 500–1000 °C (l). The reaction



is weakly exothermic, and requires a high reaction temperature, so that the oxygen must also be heated to > 1000 °C (m). This can be achieved with an electric plasma flame, by reacting part of the oxygen with carbon monoxide, or by indirect heating. Hot TiCl_4 and oxygen (110–150% of the stoichiometric amount) are fed separately into a reaction chamber where they must be mixed as rapidly and completely as possible to give a high reaction rate. For this reason, and also because the TiO_2 has a strong tendency to cake onto the walls [89–91], many different reactor designs have been proposed and used. The same considerations apply to the cooling unit (o) where the pigment is very rapidly cooled to below 600 °C. Cooling zones of various geometries are used. If caking occurs, the material can be removed by introducing abrasive particles [92].

The mixture of gases (Cl_2 , O_2 , CO_2) and pigment can be further cooled during dry separation of the pigment either indirectly or directly by solid particles, e.g., sand. The pigment-containing gas is then filtered (p). The gas stream is recycled to the cooling zone (o) of the combustion furnace and to the chlorination process as oxygen-containing chlorine via the liquefaction unit (u). The chlorine adsorbed on the pigment can be removed by heating or by flushing with nitrogen or air.

The wet separation process, in which the pigment-containing gas mixture (Cl_2 , O_2 , and CO_2) is quenched in water, has not become established.

22.7.3.3 Pigment Quality

The quality of the TiO_2 pigment is influenced by various factors. Reaction temperature, excess oxygen, and flow conditions in

the reactor affect particle size and size distribution. Therefore, optimum conditions must be established for every reactor design. Caking of the TiO_2 on the walls of the reactor leads to impairment of quality.

The presence of water during combustion of the TiCl_4 gives rise to nuclei which promote the formation of finely divided pigment particles. It can be added directly to the oxygen or can be produced by the combustion of hydrogen-containing materials.

The presence of AlCl_3 promotes the formation of rutile and a more finely divided pigment. It is added in amounts of up to 5 mol%. Many methods have been proposed for rapidly generating and directly introducing the AlCl_3 vapor into the TiCl_4 vapor. Addition of PCl_3 and SiCl_4 suppresses rutile formation, so that anatase pigment is obtained [93]. However, pigments of this type have not appeared on the market.

Pigments produced by the chloride process (chloride pigments) have better lightness and a more neutral hue than pigments produced by the sulfate process (sulfate pigments). Pigments used in demanding applications are almost always subjected to inorganic aftertreatment.

22.7.3.4 Aftertreatment

Aftertreatment of the pigment particles improves the weather resistance and lightfastness of the pigmented organic matrix, and dispersibility in this matrix. The treatment consists of coating the individual pigment particles with colorless inorganic compounds of low solubility by precipitating them onto the surface. However, this reduces the optical performance of the pigment approximately in proportion to the decrease in the TiO_2 content. The surface coatings prevent direct contact between the binder matrix and the reactive surface of the TiO_2 . The effectiveness of these coatings largely depends on their composition and method of application, which may give too porous or too dense a coating. The treatment process also affects the dispersibility of the pigment, and therefore a compromise of-

ten has to be made. High weather resistance and good dispersibility of the pigment in the binder or matrix are usually desired. These effects are controlled by using different coating densities and porosities. Other organic substances can be added during the final milling of the dried pigment.

Several types of treatment are used:

- Deposition from the gas phase by hydrolysis or decomposition of volatile substances such as chlorides or organometallic compounds. Precipitation onto the pigment surface is brought about by adding water vapor. This method is especially applicable to chloride pigments, which are formed under dry conditions.
- Addition of oxides hydroxides or substances that can be adsorbed onto the surface during pigment grinding. This can produce partial coating of the pigment surface.
- Precipitation of the coating from aqueous solutions onto the suspended TiO_2 particles. Batch processes in stirred tanks are preferred; various compounds are deposited one after the other under optimum conditions. There is a very extensive patent literature on this subject. Continuous precipitation is sometimes used in mixing lines or cascades of stirred tanks. Coatings of widely differing compounds are produced in a variety of sequences. The most common are oxides, oxide hydrates, silicates, and/or phosphates of titanium, zirconium, silicon, and aluminum. For special applications, boron, tin, zinc, cerium, manganese, antimony, or vanadium compounds can be used [94, 95].

Three groups of pigments have very good lightfastness or weather resistance:

- Pigments with dense surface coatings for paints or plastics formed by:
 - Homogeneous precipitation of SiO_2 with precise control of temperature, pH, and precipitation rate [96]: ca. 88% TiO_2
 - Two complete aftertreatments, calcination is performed at 500–800 °C after the first

or second aftertreatment [97]: ca. 91% TiO_2

– Aftertreatment with Zr, Ti, Al, and Si compounds, sometimes followed by calcination at 700–800 °C [98]: ca. 95% TiO_2

- Pigments with porous coatings for use in emulsion paints obtained by simple treatment with Ti, Al, and Si compounds, giving a silica content of 10% and a TiO_2 content of 80–85%
- Lightfast pigments with dense surface coatings for the paper industry that have a stabilized lattice and a surface coating based on silicates or phosphates of titanium, zirconium, and aluminum: ca. 90% TiO_2

Coprecipitation of special cations such as antimony or cerium can improve lightfastness further [99]. After treatment in aqueous media, the pigments are washed on a rotary vacuum filter until they are free of salt, and then dried using, e.g., belt, spray, or fluidized-bed dryers.

Before micronizing the pigment in air-jet or steam-jet mills, and sometimes also before drying, the pigment surface is improved by adding substances to improve dispersibility and facilitate further processing. The choice of compounds used, which are mostly organic, depends on the intended use of the pigment. The final surface can be made either hydrophobic (e.g., using silicones, organophosphates, and alkyl phthalates) or hydrophilic (e.g., using alcohols, esters, ethers and their polymers, amines, organic acids). Combinations of hydrophobic and hydrophilic substances have proved especially useful for obtaining surface properties that give better dispersibility and longer shelf life [100].

22.7.3.5 Problems with Aqueous and Gaseous Waste

Aqueous Waste. In the *sulfate process*, 2.4–3.5 t concentrated H_2SO_4 are used per tonne of

TiO_2 produced, depending on the raw material. During processing, some of this sulfuric acid is converted to sulfate, primarily iron(II) sulfate, the rest is obtained as free sulfuric acid (weak acid). Filtration of the hydrolysate suspension can be carried out to give 70–95% of the SO_4^{2-} in a weak acid fraction containing ca. 20–25% free acid, the remaining sulfate (5–30%) is highly diluted with wash-water.

It has so far been common practice to discharge the waste acid directly into the open sea or coastal waters. If required by law, the acid is conveyed by ship to the open sea and discharged under supervision. The weak acid problem has been the subject of public discussion and criticism. As a result the discharge of weak acid into open waters will decline and eventually stop. Precipitation of the waste sulfuric acid as gypsum does not eliminate the wastewater problem because it is then necessary to dispose of large quantities of solid waste (gypsum) for which there is insufficient demand.

A process has been demonstrated in which both the free and the bound sulfuric acid (as metal sulfates) can be recovered from the weak acid in the calcination furnace (k, Figure 22.5) and in metal sulfate calcination (Figure 22.6). The process consists of two stages:

- Concentration and recovery of the free acid by evaporation
- Thermal decomposition of the metal sulfates and production of sulfuric acid from the resulting sulfur dioxide

As a result of energy requirements only acid containing > 20% H_2SO_4 can be economically recovered by evaporation. The weak acid is concentrated from ca. 20–25% to ca. 28% with minimum heat (i.e., energy) consumption, e.g., by using waste heat from sulfuric acid produced by the contact process [101], or from the waste gases from the calcination kilns used in TiO_2 production [102] (Figure 22.6).

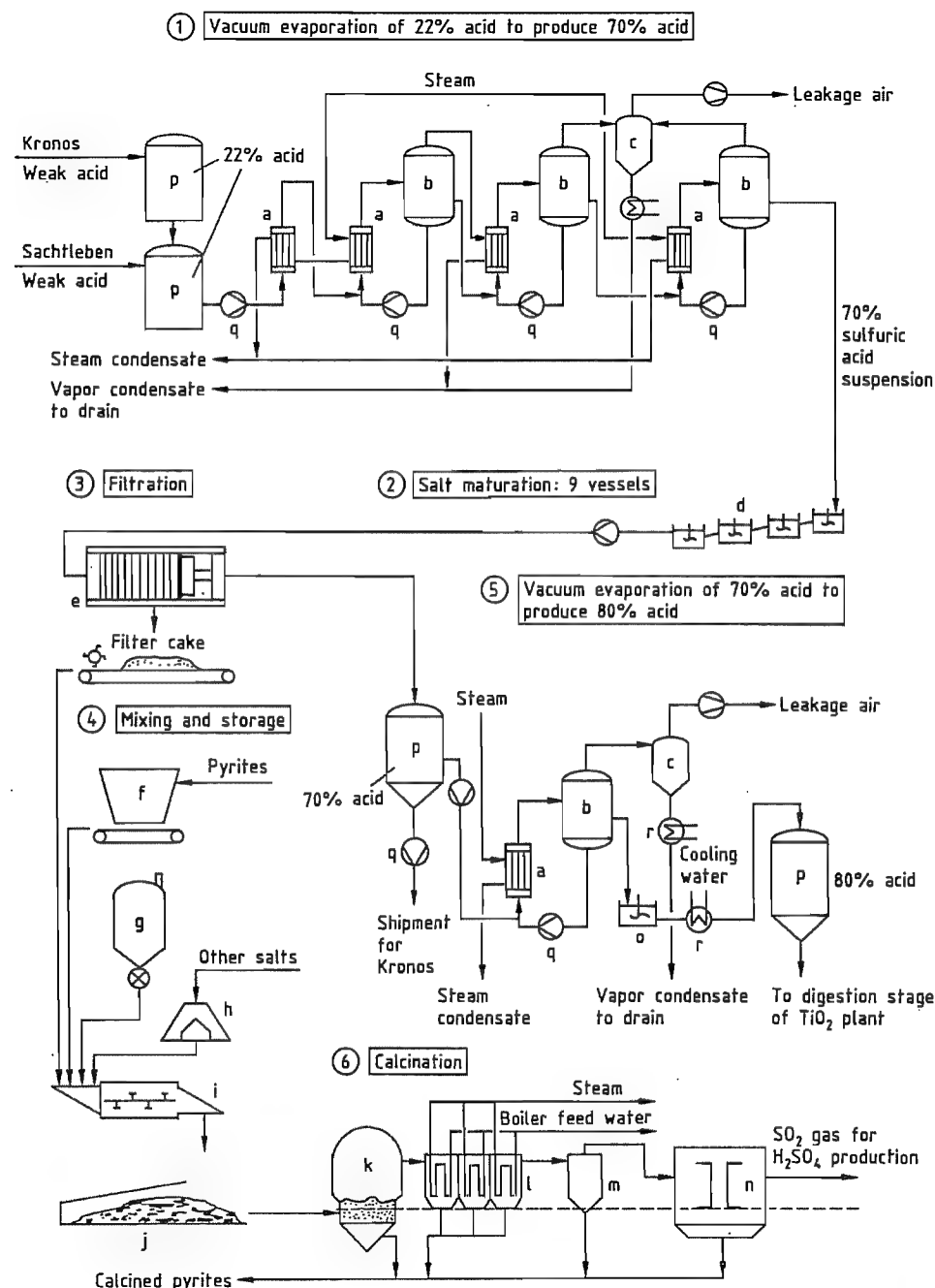


Figure 22.5: Weak acid recovery plant used by Sachtleben Chemie (based on know-how of Bayer AG): a) Heat exchanger; b) Evaporator; c) Injection condenser; d) Stirred salt maturing vessels; e) Filter press; f) Bunker for pyrites; g) Coal silo; h) Bunker; i) Mixing screw unit; j) Covered store for mixed filter cake; k) Calcination furnace; l) Waste-heat boiler; m) Cyclone; n) Electrostatic precipitator; o) Stirred tank; p) Storage tank; q) Pump; r) Cooler.

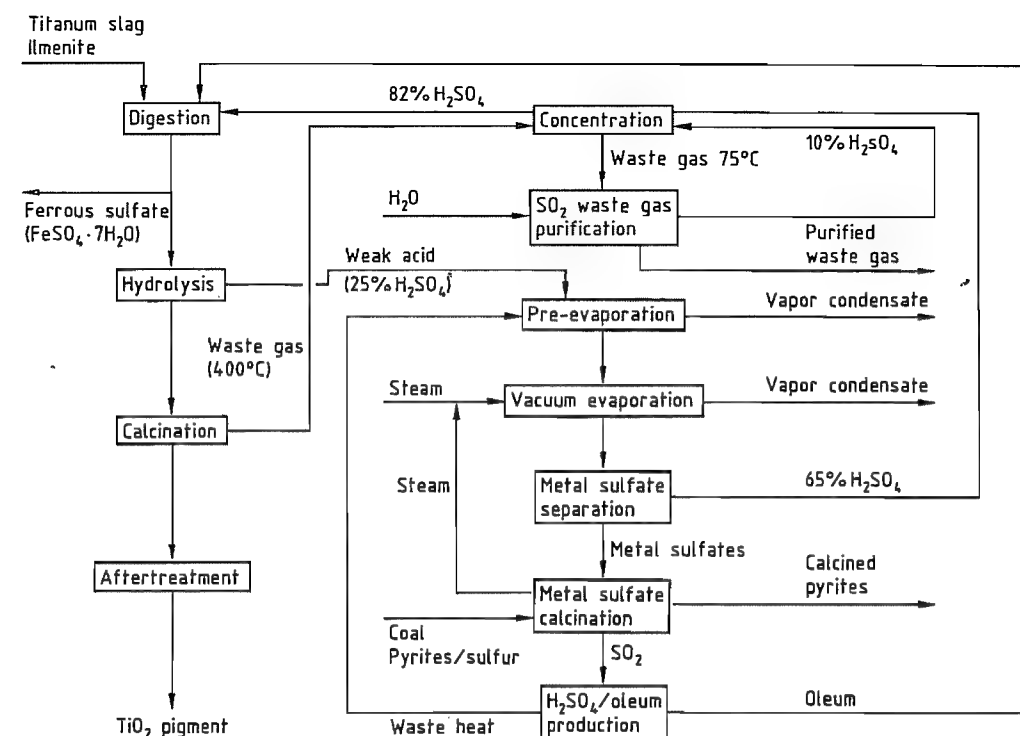


Figure 22.6: Waste heat recovery and sulfuric acid recycling during weak acid treatment (Bayer AG).

Following preliminary evaporation, further concentration is carried out in multi-effect vacuum evaporators. Since the water vapor pressure decreases strongly as the H_2SO_4 concentration increases, in general only two-stage evaporation can effectively exploit the water vapor as a heating medium. Evaporation produces a suspension of metal sulfates in 60–70% sulfuric acid (stage 1 in Figure 22.5). The suspension is cooled to 40–60 °C in a series of stirred tanks (stage 2, d) [103], giving a product with good filtering properties and an acid of suitable quality for recycling to the digestion process. Filtration (stage 3, e) is usually carried out with pressure filters [104] because they give a filter cake with an extremely low residual liquid content.

The concentration of the acid recycled to the digestion process depends on the quality of the titanium-containing raw material. For raw materials with a high titanium content, the 65–70% sulfuric acid separated from the metal

sulfates must be further concentrated to give 80–87% acid (stage 5).

Concentration can be carried out in steam-heated vacuum evaporators, or by using the heat from the TiO_2 calcination kilns [105]. Cooling the acid obtained after this concentration process yields a suspension of metal sulfates that can be directly used for digestion of the raw material. The metal sulfates recovered from the sulfuric acid in stage 3 are moist because they contain 65–70% sulfuric acid; they therefore have no direct use. They can be converted to a disposable material by reaction with calcium compounds [106]. Thermal decomposition of the metal sulfates to form the metal oxides, sulfur dioxide, water, and oxygen is energy intensive, but is advantageous from the ecological point of view. The energy requirement is ca. 4×10^9 J per tonne of filter cake. Thermal decomposition is carried out at 850–1100 °C in a fluidized-bed furnace (stage 6). The energy is supplied by coal, pyrites, or

sulfur. The sulfur dioxide produced by the thermal decomposition is purified by the usual methods, dried, and converted into sulfuric acid or oleum. This pure acid or oleum is mixed with the recovered sulfuric acid and used in the digestion process.

The metal oxides produced by thermal decomposition contain all the elements initially present in the raw material apart from the titanium which has been converted into pigment. The mixture of metal oxides, mainly iron oxide, can be used as an additive in the cement industry if demand exists.

The continually increasing demand for environmentally friendly industrial processes has also led to the development of techniques for recycling of the acidic wash water. In the *chloride process*, wastewater problems arise if the raw material contains < 90% TiO₂. The metal chloride by-products are sometimes disposed of in solution by the "deep well" method (e.g., at Du Pont). The metal chloride solutions are pumped via deep boreholes into porous geological strata. Special geological formations are necessary to avoid contamination of the groundwater by impurities.

Increasing restrictions also apply to the chloride process, so that efforts are continually being made to use the iron chloride by-product, e.g., in water treatment and as a flocculation agent.

Waste Gas Problems. The gases produced in the calcination kiln are cooled in a heat exchanger, and entrained pigment is removed, washed, and recycled to the process. The SO₂ and SO₃ formed during calcination are then scrubbed from the gases to form dilute sulfuric acid which is recycled.

22.7.4 Economic Aspects

The burning of TiCl₄ with oxygen or the calcination of TiO₂ hydrolysates produces either anatase or rutile pigments, depending on the doping and lattice stabilization. They are marketed directly or after being coated with oxides or hydroxides of various elements. Different treatments are necessary depending on the field of application, and all major pigment

producers have a large number of pigment grades. Product groups are listed in Table 22.11. Pigments of all grades are available with or without organic treatment. Over 400 different TiO₂ pigment grades are currently on the market. Table 22.12 gives the capacities and processes of the most important pigment producers.

Table 22.11: Classification of TiO₂ pigments according to composition (DIN draft specification E 55912, sheet 2, issue 4075).

Pigment	Class	TiO ₂ (min.), %	Water-solu- ble salts, %	Volatiles (max.), %
Anatase (Type A)	A1	98	0.6	0.5
	A2	92	0.5	0.8
Rutile R1 (Type R)		97	0.6	0.5
	R2	90	0.5	1.5
	R3	80	0.7	2.5

There have been few increases in production capacity since the early 1980s resulting in a titanium dioxide shortage. A considerable increase of capacity is planned by debottlenecking and building new plants. The proposed expansions reported in the literature indicate that capacity will increase to 4 × 10⁶ t by 1995 [58].

Powdered TiO₂ pigments are usually supplied in 25 kg sacks (50 lbs, USA) or in large bags containing 0.5–1 t pigment. Aqueous suspensions with solids contents of 68–75% are also available and have great advantages as regards the distribution and metering of the pigment in aqueous systems. The dust formation that occurs with dry pigment is also avoided. With the development of products with improved flow properties and modern pneumatic delivery technology, supply in silo wagons is becoming increasingly important.

22.7.5 Pigment Properties

The pigment properties are extremely important when TiO₂ is used as a white pigment; they include lightening power, hiding power, lightness, hue, gloss formation, gloss haze, dispersibility, lightfastness, and weather resistance. These properties are a function of chemical purity, lattice stabilization, particle size and size distribution, and the coating pro-

duced by aftertreatment. They also depend on the medium and cannot generally be accurately described in scientific terms. Some of the important properties of TiO₂ pigments are described below.

Scattering Power. The refractive indices of rutile and anatase are very high (2.70 and 2.55, respectively). Even after incorporation in a wide range of binders, they lie in the range between 1.33 (water) and 1.73 (polyester fibers). The scattering power depends on the particle size, and for TiO₂ is at its maximum at a particle size of 0.2 μm (Mie's theory) [107]. The scattering power also depends on the wavelength; TiO₂ pigment particles with a size < 0.2 μm scatter light of shorter wavelengths more strongly and therefore show a slight blue tinge, while larger particles have a yellow tone.

Hue. The whiteness (lightness and hue) of TiO₂ pigments depends primarily on the crystalline modification, the purity, and the particle size of the TiO₂ (see above). As the absorption band (385 nm) of anatase pigments is shifted into the UV region, compared with rutile pigments they have less yellow undertone. Any transition elements present in the crystal structure have an adverse effect on the whiteness, so manufacturing conditions are of the greatest importance. Thus, pigments produced by the chloride process (which includes distillative purification of TiCl₄ before the combustion stage) have a higher color purity and very high lightness values.

Dispersion. Good disintegration and dispersion of the TiO₂ pigments in the medium are necessary to obtain high gloss and low gloss haze. These requirements are satisfied by intensive grinding and by coating the pigment surface with organic compounds. The compounds used for this surface treatment depend on the field of application.

Lightfastness and Weather Resistance. Weathering of paints and coatings containing TiO₂ leads to pigment chalking [108]. If weathering occurs in the absence of oxygen,

or in binders with low permeability to oxygen (e.g., in melamine formaldehyde resins), no chalking is observed, but graying takes place, which decreases on exposure to air. Graying is greatly reduced in the absence of water. Both effects are more severe with anatase pigments. Empirical stabilization processes have been developed by pigment producers, e.g., doping with zinc or aluminum prior to calcination.

According to modern theories, impairment of the lightfastness and weather resistance of TiO₂ pigments proceeds according to the following cycle [109]:

1. Molecules of water are bound to the TiO₂ surface forming hydroxyl groups on the surface.
2. Absorption of light of short wavelength (anatase < 385 nm, rutile < 415 nm) occurs, producing an electron and an electron defect or "hole" (exciton) in the crystal lattice which migrate to the surface of the pigment.
3. At the surface of the pigment, an OH⁻ ion is oxidized to an OH[•] radical by an electron "hole". The OH⁻ ion is then desorbed and can oxidatively break down the binder. A Ti³⁺ ion is simultaneously produced by reduction of Ti⁴⁺ with the remaining electron of the exciton.
4. The Ti³⁺ ion can be oxidized by adsorbed oxygen with formation of an O₂⁻ ion. The latter reacts with H⁺ and is converted into an HO₂[•] radical.
5. The cycle ends with the binding of water to the regenerated TiO₂ surface.

The chalking process can be regarded as the reaction of water and oxygen to form OH[•] and HO₂[•] radicals under the influence of shortwave radiation and the catalytic activity of the TiO₂ surface:

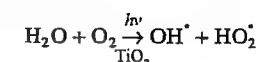


Table 22.12: World TiO₂ pigment producers (1988).

Country	Company	Location	Capacity, 10 ³ t/a			
			Chloride	Sulfate	Total	
United States	Du Pont	New Johnsonville	250		545	
		De Lisle	141			
		Edge Moore	119			
		Antioch	36			
	SCM Corporation	Baltimore	45	60	196	
		Ashtabula	47	44		
		Savannah	52	48	100	
		Hamilton	78		78	
Canada	Kemira Oy	Varenes	40	36	76	
	NL Chemicals Incorporated	Tracy		42	42	
	Tioxide Canada					
Brazil	Titanio do Brasil/Bayer	Salvador		54	54	
Mexico	Du Pont	Tampico	60		60	
Total, America					1151	
Germany	Kronos Titan	Leverkusen	80	35	175	
		Nordenham				
		Krefeld-Urdigen				
		Duisburg-Homberg				
United Kingdom	Tioxide UK	Grimsby	50	105	155	
	SCM Chemicals	Stallingborough	78	31	109	
France	Thann et Mulhouse (Rhône-Poulenc)	Le Havre		95	125	
				30		
				80	80	
Finland	Kemira Oy	Calais		80	80	
Italy	Tioxide Italia	Pori		80	80	
Belgium	Kronos Titan	Scarline		75	75	
		Langebrügge		40	40	
		Bayer		30	30	
Spain	Tioxide España	Huelva		65	65	
Netherlands	TDF Tiofine	Botlek		39	39	
Norway	Kronos Titan	Fredrikstad		27	27	
Total, Western Europe					1145	
Soviet Union	state-owned	numerous plants		100	100	
Poland	ZPN	Police		36	36	
Yugoslavia	Cinkarne Celje	Celje		28	28	
Czechoslovakia	Prerovske Chemiske	Prerov		22	22	
Total, Eastern Europe					186	
South Africa	SA Tioxide	Umbogwintwini		35	35	
Total Africa					35	
Australia	SCM Chemical	Australind		36	36	
	Tioxide Australia	Burnie		35	35	
Total, Australia					71	
Japan	Ishibara Sangyo Kaisha	Yokkaichi	38	92	130	
		Teikoku Kako		42	42	
		Sakai Chemical		37	37	
		Furukawa Mining		18	18	
		Fuji Titanium		16	16	
		Titan Kogyo		16	16	
		Hakusai Chemical		15	15	
		Tohoku Chemical		11	11	
Total, Japan					285	
India	Kerala Minerals & Metals	Kerala	22		22	
		Trivandrum		13	13	
China	state-owned	numerous plants		25	25	
South Korea	Hankuk Titanium	Young Dung Po		18	18	
Taiwan	China Metal & Chemicals	Chin Shin		(6)	(6)	
		Chin Shin				
		ISK Taiwan, Ishibara				
Total, Far East (excluding Japan)					88	
Total world capacity			1135	1826	2961	

The enthalpy requirement for this reaction (312 kJ/mol) is provided by radiation of wavelength 385 nm. The cycle (1)–(5) is broken by excluding air or water. If oxygen is excluded or a binder is chosen in which the diffusion of oxygen is rate determining, a concentration of Ti³⁺ ions builds up. Graying then takes place, but this decreases with gradual exposure to oxygen. If water is excluded, rehydration and formation of surface hydroxyl groups do not take place; breakdown of the binder therefore ceases. Despite this photochemical breakdown of the binder, treated rutile pigments are used to stabilize many binders. This is because non-pigmented coatings are degraded by exposure to light and weathering; the added TiO₂ pigments prevent light from penetrating the deeper layers of the coating film and thus inhibit breakdown of the binder. High-quality TiO₂ pigments must satisfy stringent requirements with respect to weather resistance. They must withstand the severe climatic conditions of the Florida test, resisting a two-year exposure without appreciable chalking or deterioration of gloss.

22.7.6 Analysis

The crystal structure of the pigments is determined by X-ray analysis which is sensitive enough to determine 0.3–0.5% anatase in the presence of 99.7–99.5% rutile.

A qualitative test for TiO₂ is a blue violet coloration of beads of microcosmic salt (NaNH₄HPO₄·4H₂O), or a yellow orange coloration produced when hydrogen peroxide is added to a test solution in hot, concentrated sulfuric acid containing ammonium sulfate. For quantitative determination, the pigment is dissolved or digested in sulfuric acid and the solution is reduced to Ti³⁺ with cadmium, zinc, or aluminum. The Ti³⁺ ions are then usually titrated with a standard solution of iron(III) ammonium sulfate solution, with potassium rhodanide as an indicator, or using potentiometric end point determination.

Impurities can be determined by wet analysis, X-ray fluorescence, or spectrographic analysis (e.g., atomic absorption).

Typical analysis figures for an untreated rutile pigment are TiO₂ 99.4%, K₂O 0.24%, P₂O₅ 0.21%, Fe₂O₃ 40 ppm, Sb₂O₃ 24 ppm, Al₂O₃ 20 ppm, Mg 5 ppm, Zn 3 ppm, Cr 2 ppm, Mn, Cu, Hg, Cd, Co, Ni, Se, Sn, Ag < 1 ppm.

Table 22.13: Consumption of TiO₂ pigments in 1987 (10³ t) [58].

Use	United States	Western Europe	Asia and Pacific	Rest of world	World total
Coatings	466	453	285	361	1565
Paper	259	91	24	49	423
Plastics	172	154	65	77	479
Other	54	82	109	60	305
Total	951	780	494	547	2772
Use per capita, kg	4.2	2.3	0.2	0.2	0.5

Table 22.14: Predicted percentage annual growth rates for use of TiO₂ (1986–1992) [103].

End use	United States	Western Europe	Asia and Pacific	Rest of world	World total
Coatings	1.0	1.0	4.5	2.0	1.5
Paper	2.5	2.0	2.0	1.5	2.5
Plastics	4.0	3.5	6.0	4.0	4.0
Other	0.5	1.0	1.0	2.0	1.0
Total	2.0	1.7	4.3	2.1	2.3

22.7.7 Uses of Pigmentary TiO₂

Titanium dioxide is used universally, having almost completely replaced other white pigments. Consumption figures for 1987 are given in Table 22.13 [58]. The greatest annual increase in use has been for coloring plastics (> 4%), followed by the coloring of paper (ca. 2.5%). Geographically, the increase in consumption of TiO₂ has been the greatest in Asia (Table 22.14).

Paints and coatings amount for the largest volume of TiO₂ production. The presence of the pigment enables the protective potential of the coating material to be fully exploited. As a result of continuing developments in TiO₂ pigments, coatings only a few micrometers thick fully cover the substrate. Commercially available pigments permit paint manufacture with simple dispersion equipment, such as disk dispersers. Organic treatment prior to steam jet micronization yields pigments with improved gloss properties and reduced gloss haze for

use in stoving enamels. Sedimentation does not occur when these products are stored, and they possess good lightfastness and weather resistance.

Printing Inks. Modern printing processes operate at coating thicknesses of $< 10 \mu\text{m}$, and therefore require the finest possible TiO_2 pigments. These very low film thicknesses are only possible with TiO_2 pigments that have a lightening (reducing) power seven times that of lithopone. Because of its neutral hue, TiO_2 is especially suitable for lightening (reducing) colored pigments.

Plastics. Titanium dioxide is used to color plastic packaging films $< 100 \mu\text{m}$ thick. This coloring is required by the customer to hide the packaged goods from view, and to allow the film to be printed for advertising and information purposes. Furthermore, TiO_2 pigments absorb UV radiation with a wavelength $< 415 \text{ nm}$ and thus protect the packaged goods from these harmful rays which could, for example, reduce the storage life of fat-containing food.

Fibers. Titanium dioxide pigments give a matt appearance to synthetic fibers, eliminating the greasy appearance caused by their translucent properties. Anatase pigments are used for this because their abrasive effect on the spinning operation is about one quarter that of the rutile pigments. The poor lightfastness of anatase pigments in polyamide fibers can be improved by treatment with manganese or vanadium phosphate.

Paper. In Europe, fillers such as kaolin, chalk, or talc are preferred as brightening agents and opacifiers in paper manufacture. Titanium dioxide pigments are suitable for very white paper that has to be opaque even when very thin (air mail or thin printing paper). The TiO_2 can be incorporated into the body of the paper or applied as a coating to give a superior quality ("art" paper).

Laminated papers are usually colored with extremely lightfast rutile pigments before being impregnated with melamine urea resin for use as decorative layers or films.

Other areas of application for TiO_2 pigments include the enamel and ceramic industries, the manufacture of white cement, and the coloring of rubber and linoleum.

Titanium dioxide pigments are also used as UV absorbers in sunscreen products, soaps, cosmetic powders, creams, toothpaste, cigar wrappers, and in the cosmetics industry. Their most important properties are their lack of toxicity, compatibility with skin and mucous membranes, and good dispersibility in organic and inorganic solutions and binders.

Electrically conducting TiO_2 pigments have been produced by an aftertreatment to give a coating of mixed oxides of indium and tin, or antimony and tin [110]. These pigments are applied to fibers used in photosensitive papers for electrophotography, and for the production of antistatic plastics.

22.7.8 Uses of Nonpigmentary TiO_2

A number of industrial products require TiO_2 starting materials with well-defined properties for a specific application. Some of the most important of these grades of titanium dioxide are those with a high specific surface area, a small particle size, and very high reactivity. Stringent requirements often exist regarding purity and property consistency. The world consumption of this nonpigmentary TiO_2 in 1990 was ca. 110 000 t and was broken down as follows:

Enamels ceramics	28 000 t
Glass, glass ceramics	26 000 t
Electroceramics	14 000 t
Catalysts and catalyst supports	10 000 t
Welding fluxes	10 000 t
Colored pigments (lightfast pigments)	9 000 t
Electrical conductors	5 000 t
Titanium boride and carbide	300 t
Potassium hexafluorotitanate	2 000 t
Optical glasses	1 000 t
Potassium titanate	1 000 t
Standard ceramics	500 t
Refractory coatings	200 t
UV-screening	100 t

The annual growth rate in these markets is expected to be a few per cent. Growth could be higher if catalysts for environmental protection become mandatory, or if rutile mixed-

phase pigments seem likely to replace other pigments thought to have toxic properties

Electroceramics. Titanates prepared from finely divided, high-purity TiO_2 hydrolysates are used in capacitors and piezoelectric materials. The specifications of the TiO_2 starting materials with respect to purity, reactivity, and sintering properties are expected to become more stringent.

Catalysts. The main area of application for TiO_2 is in catalysts for the removal of nitrogen oxides from waste gases from power stations and industry. The nitrogen oxides in the waste gas are reacted with ammonia in the presence of oxygen on the catalyst to form nitrogen and water (Selective Catalytic Reduction) [111]. The first equipment of this type is now in operation in Germany and Japan. Increasing demand is expected following reductions in permitted levels of emission, the spread of these ideas to other countries, and maintenance requirements during operation. In addition to TiO_2 the catalysts usually contain ca. 10% tungsten oxide and ca. 1% V_2O_5 , and are extruded into a honeycomb shape. The TiO_2 has high specifications with respect to purity, particle size, and porosity to ensure that the desired catalytic activity is obtained.

Mixed Metal Oxide Pigments. The starting material is a TiO_2 hydrolysate, which is calcined with oxides of transition metals to form chromium rutile or nickel rutile pigments. Depending on the particle size, pigments with various shades of yellow are produced. These pigments should have considerable growth potential on account of their quality and environmental safety.

UV Absorption. Finely divided TiO_2 pigments are used as sunscreens in the cosmetic industry. Intensive research work is in progress worldwide aimed at utilizing the photoactivity of TiO_2 . Titanium dioxide catalyzes the decomposition of organic compounds in wastewater; water is decomposed into hydrogen and oxygen in the presence of sunlight.

22.7.9 Toxicology

Titanium dioxide is highly stable and is regarded as completely nontoxic. Investigations on animals which have been fed TiO_2 over a long period give no indication of titanium uptake [112]. Absorption of finely divided TiO_2 Pigments in the lungs does not have any carcinogenic effect [113].

22.7.10 Rutile Mixed Metal Oxide Pigments

The rutile (TiO_2) lattice offers considerable scope for variation [114]. In this lattice, titanium ions are surrounded by six neighboring oxygen atoms at the corners of a regular, but slightly distorted octahedron. Colored pigments may be obtained by substituting transition-metal ions for the titanium ions [115]. If the colored cation substituent is not tetravalent, another cation of appropriate valency must be substituted into the rutile lattice to maintain an average cation valency of four.

H. H. SCHAUMANN prepared the first mixed-phase rutile pigments by incorporating nickel oxide and antimony oxide into rutile to give a yellow pigment, and cobalt and antimony oxides to give an ochre pigment [116]. Other rutile mixed metal oxide phases were first used as ceramic colorants (e.g., with chromium-tungsten, brown [117]) or for coloring porcelain enamels (e.g., with copper-antimony, lemon yellow; manganese-antimony, dark brown; iron antimony, gray [118]; and vanadium-antimony, dark gray). In commercial mixed-phase rutile pigments, between 10 and 20 mol% of the titanium ions are replaced by substituent metal ions.

Nickel and chromium mixed-phase rutile pigments are industrially important. When nickel and chromium are substituted into the rutile lattice, higher valency metals (e.g., antimony, niobium, or tungsten) must also be substituted to maintain an average valency of four.

Nickel rutile yellow, C.I. Pigment Yellow 53:77788, is a light lemon yellow pigment with the approximate composition

($\text{Ti}_{0.85}\text{Sb}_{0.10}\text{Ni}_{0.05}\text{O}_2$). Antimony can be replaced by niobium without any appreciable change in color [119].

Chromium rutile yellow pigments, C.I. Pigment Brown 24:77310, usually contain antimony to balance the valency. Their composition is approximately ($\text{Ti}_{0.90}\text{Sb}_{0.05}\text{Cr}_{0.05}\text{O}_2$). Depending on particle size, the color varies from light to medium ochre (buff). Stability towards plastics at high temperature is considerably improved by the incorporation of small quantities of lithium [120] or magnesium [121]. If antimony is replaced by tungsten, the products become darker in color, whereas replacement by niobium leaves the color unchanged.

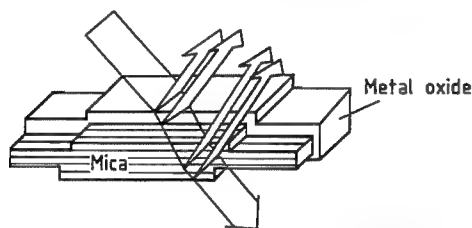


Figure 22.7: Simplified scheme of light reflection at the phase boundaries of a metal oxide-mica pigment.

22.7.11 Titanium Dioxide-Mica Pigment [122–127]

The dominant class of nacreous pigments is based on platelets of natural mica coated with thin films of transparent metal oxides (Figure 22.7). Mica minerals are sheet layer silicates. Nacreous pigments are usually based on transparent muscovite but some are based on dark brown phlogopite. Although muscovite occurs worldwide, few deposits are suitable for pigments; it is biologically inert and approved for use as a filler and colorant.

Selection and workup of the mica substrate are two of the key factors which determine the quality and appearance of nacreous pigments [124–127]. The aspect ratio of the final pigment depends on the particle size distribution of the mica platelets which have a thickness of 300–600 nm and various diameter ranges (e.g., 5–25, 10–50, 30–110 nes of the metal oxide-coated mica and scattered from the

edges, brilliance and hiding power are inversely related to each other.

A mica pigment coated with a metal oxide has three layers with different refractive indices and four phase boundaries P_1 – P_4 : (P_1) TiO_2 (P_2) mica (P_3) TiO_2 (P_4) (Figure 22.8). Interference of light is generated by reflections of all six combinations of phase boundaries, some of which are equal: $P_1P_2 = P_3P_4$, $P_1P_3 = P_2P_4$, P_1P_4 , and P_2P_3 . The thickness of the mica platelets varies in accordance with a statistical distribution. Consequently, interference effects involving the phase boundaries between the mica substrate and the oxide coating add together to give a white background reflectance. The interference color of a large number of particles therefore depends only on the thickness of the upper and lower metal oxide coating layers [122–127].

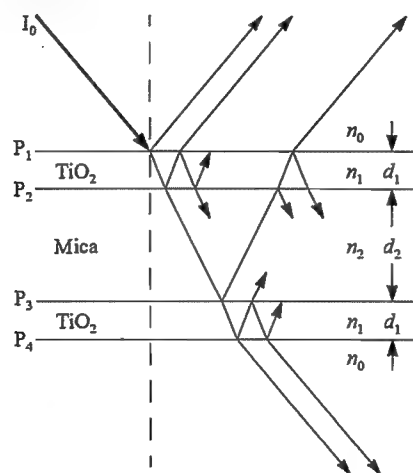


Figure 22.8: Multilayer, thin-film pigment consisting of a TiO_2 coating (high n_1) surrounding a mica platelet (low n_2). The four phase boundaries (P_1 – P_4) are indicated.

The development of the mica-based pigments started with pearlescent colors (Figure 22.9A, TiO_2 -mica). It was followed by brilliant, mass-tone-colored combination pigments (i.e., mica, TiO_2 , and another metal oxide) with one color (interference color same as mass tone) or two colors (interference and mass tone different) that depend on composition and viewing angle (Figure 22.9B). In the 1980s further development was made by coat-

ing mica particles with transparent layers of iron(III) oxide (Figure 22.9C).

The first multilayer pigments were marketed in the 1960s as TiO_2 -coated muscovite

miccas [122–127]. Two different processes are used for coating mica in aqueous suspension on a commercial basis:

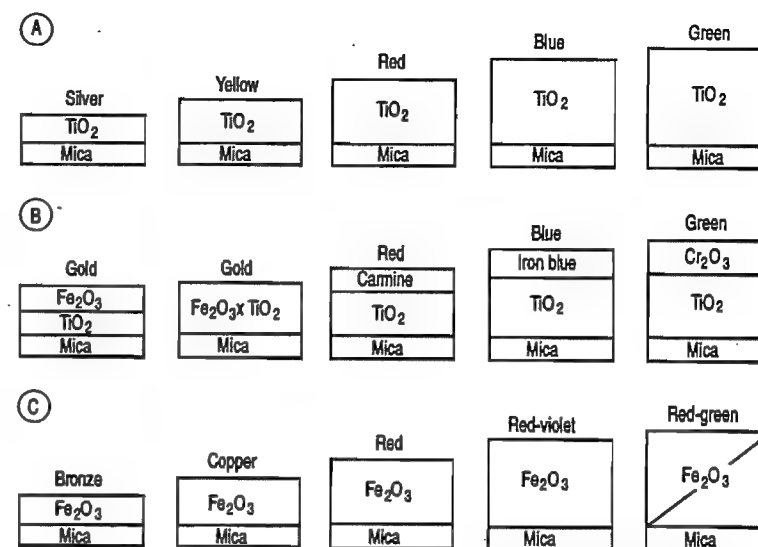


Figure 22.9: Upper half of metal oxide-mica pigments. Increasing layer thickness of metal oxide causes different interference colors in reflection. Combination with absorption colorants (e.g., Fe_2O_3) produces metallic effects. A) Interference colors; B) Combination pigments; C) Metallic colors.

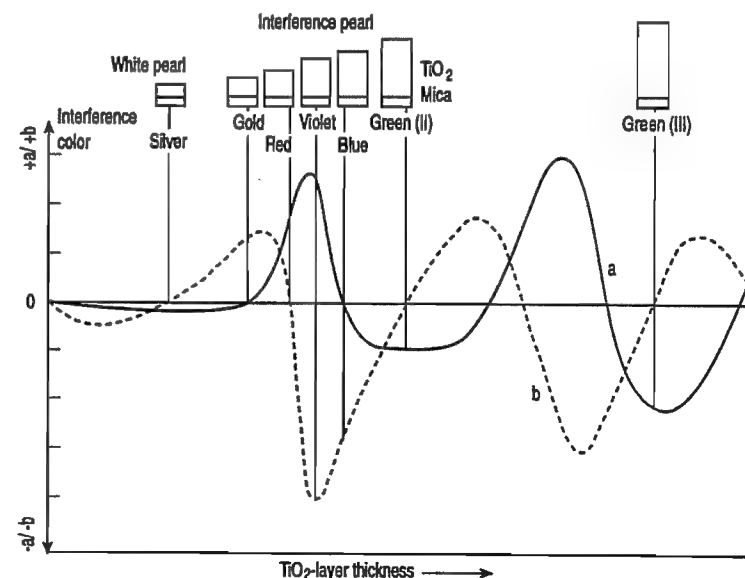
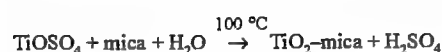
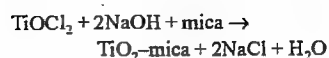


Figure 22.10: Experimental dependence of interference colors on the TiO_2 layer thickness on mica expressed in the Hunter $L a b$ scale (a, b only).

● Homogeneous hydrolysis (sulfate process)

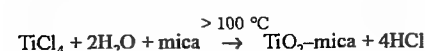


● Titration (chloride process)



The pigments are then dried and calcined at 700–900 °C. The titration process is preferred for interference pigments with thick TiO₂ layers because it is easier to control.

Chemical vapor deposition in a fluidized bed has also been proposed [128, 129]:



Only the TiO₂ anatase crystal modification is formed on the mica surface. Small amounts of SnO₂ are therefore used to catalyze conversion to the rutile structure with its higher refractive index, brilliance, color intensity, and superior weather resistance.

The sequence of interference colors obtained with increasing TiO₂ layer thickness agrees with theoretical calculations in the color space. An experimental development of *L a b* values is given in Figure 22.10.

TiO₂-mica pigments are used in all color formulations of conventional pigments where brilliance and luster are required in addition to color, i.e., in plastics, coatings, printing, and cosmetics. The major market for silver white pigments (pearl pigments, "white metallic") is the plastics industry.

One possibility for attractive combination pigments is the coating of TiO₂-mica pigments with an additional layer of an inorganic or organic colorant. The thickness of the TiO₂ layer is decisive for the brilliance or interference effect under regular viewing conditions whereas the transparent colorant dominates at all other viewing angles. A deep, rich color with a luster flop at all angles is attained for the case that colorant and interference color are matched. If interference color and masstone of the colorant are different, a color flop (two-tone pigments) is seen in addition to the luster flop.

Iron(III) oxide is the most important metal oxide for combination with titanium dioxide on mica flakes. Brilliant golden pigments result which can be applied for several purposes. Two routes are used to synthesize these pigments, and different structures are formed [122, 124, 125, 127]. In the first case, a thin layer of Fe₂O₃ is coated on the surface of a TiO₂-mica pigment. The overall interference color is the result of both metal oxide layers. The masstone is determined by the Fe₂O₃ layer, and interesting gold pigments (e.g., red-dish gold) are possible. In the second case, coprecipitation of iron and titanium oxide hydroxides on mica particles and calcination leads to greenish gold pigments.

Coating of TiO₂-mica pigments with an organic colorant for a masstone or two-tone pigment is done by precipitation or deposition on the pigment surface in aqueous suspension, assisted by complexation or surfactants. A second route is fixing the colorants as a mechanically stable layer using suitable additives.

Solid state reactions and CVD process enlarge the possibilities for the synthesis of modified TiO₂-mica pigments. In addition, the calcination of the materials in the presence of inert (e.g., N₂, Ar) or reactive gases (e.g., NH₃, H₂, hydrocarbons) allows the formation of phases which are not producible by working in air. Table 22.15 contains examples for TiO₂-mica-based pearlescent pigments with special coloristic properties.

Titanium dioxide-mica pigments have been developed at first only because of their excellent coloristic properties. Meanwhile, they are also interesting for functional uses. In coatings with a high content of platelet fillers, an advantageous overlapping roof-tile type arrangement is possible that provides close interparticle contact, barrier effects, and dense covering. The composition of the oxide layer on the mica surface and its thickness are always responsible for the physical properties like IR-reflexivity or laser markability. So TiO₂-mica pigments can be used for IR-reflecting plastic sheets [135] (e.g. for domed

and continuous rooflights) or for laser marking of plastics and coatings [133].

Table 22.15: Examples for mica-based pearlescent pigments with special coloristic properties.

Pigment composition	Preparation	Remarks	Ref.
TiO ₂ -x/ TiO ₂ /mica	TiO ₂ /mica + H ₂ (Ti, Si) grey, T > 900 °C (solid-state blue-grey reaction)		[130]
TiO ₂ N/ TiO ₂ /mica	TiO ₂ /mica + NH ₃ T > 900 °C (solid-state blue-grey reaction)	grey, blue-grey	[131]
FeTiO ₃ / TiO ₂ /mica	Fe ₂ O ₃ /mica + H ₂ T > 600 °C (solid-state reaction)	grey (ilmenite pigments)	[132]
TiO ₂ /C/ mica	TiOCl ₂ + C + mica (precipitation) calcination under N ₂	silver-grey, interference colors (carbon inclusion pigments)	[133]
BaSO ₄ / TiO ₂ /mica	Ba ²⁺ + SO ₄ ²⁻ + TiOCl ₂ + mica (precipitation)	low luster pigments)	[134]

22.7.12 Transparent Titanium Dioxide

Titanium dioxide can also be produced with a primary particle size of 10–30 nm, and hence shows transparent properties. Microcrystalline titanium dioxide was first mentioned in Japanese patents in 1978.

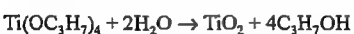
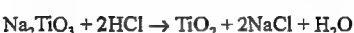
The use of micro titanium dioxide as a white pigment is limited because its light scattering is very low due to the very fine crystal size, which means that the coloring effect of conventional TiO₂ is lost. The physical properties changed significantly; there is strong UV light absorption. Consequently, such fine-particle TiO₂ is used as an UV light absorbing additive:

- for cosmetics, mainly for sunscreen formulations because of its effective UV protection over the UVC, UVB, and UVA spectrum [136];
- for automotive paints, especially in combination with aluminum flakes giving a pearlescent-like appearance; the color flop depends on the concentration of the micro

titanium dioxide in the formulation [137, 138];

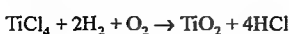
- for clear coats and wood varnishes to protect the base due to its transparency and its property to absorb UV light;
- for plastics to improve the UV durability of the polymer films itself as well as to protect UV-sensible foodstuff in plastic wrapping [139];
- as heat stabilizers in silicon rubber, as catalysts for hydrogenation [140] and oxidation [141] as well as for surface protective films for furniture and optical material [142].

Microfine TiO₂ can be obtained mainly with rutile structure by different manufacturing routes which depend on starting materials used:



The process steps include precipitation, neutralisation, filtration and washing, drying, and micronisation. Due to its small particle size the transparent titanium dioxide has a high photoactivity. To reduce this and in order to get a better weatherfastness the fine particles are coated with various combinations of inorganic oxides (e.g., silica, alumina, zirconia, iron) before drying in a similar way as that used for the conventional titanium dioxide.

Microfine TiO₂ with predominant anatase structure can also be manufactured by reductive flame hydrolysis of TiCl₄ at < 700 °C [143]:



Worldwide consumption is increasing and estimated at 1300 t/a.

Trade names include Titanium Dioxide P25 (Degussa, Germany), Hombitec RM Series (Sachtleben Chemie, Germany), and Micro Titanium Dioxide MT-Series (Tayca, Japan). Transparent titanium dioxide is also produced by Ishihara (Japan) and Kemira Oy (Finland).

22.8 Production of Titanium Tetrachloride

Titanium metal is produced exclusively by reduction of titanium tetrachloride, which is manufactured from natural rutile or from the so-called synthetic rutile obtained from ilmenite or from the TiO_2 -rich slag produced by metallurgical treatment of ilmenite (ore preparation, production of TiO_2 -rich slags, and production of synthetic rutile are described in Section 22.7.2).

The TiO_2 produced for the pigment industry by treatment of ilmenite with sulfuric acid is unsuitable as a starting material for production of the metal because of the impurities present. Also, titanium white (TiO_2) is increasingly produced from TiCl_4 . At the present time, approximately one-third of TiO_2 world production (2.1×10^6 t/a) is produced by the chloride process. Over 95% of the total quantity of titanium minerals extracted worldwide is used to produce TiO_2 pigment, and only ca. 4% for titanium metal.

In spite of the wide distribution of titanium minerals, the mining of rutile-containing ores is mainly concentrated on Australia, from which 90% of world production comes. Other important producing countries are Sierra Leone and South Africa. The most important ilmenite-producing countries are Australia (one-third of total world production) and Norway, the United States, and the Ukraine, while the leading producers of titanium slag from ilmenite are Canada and South Africa.

Chlorination of titanium dioxide is now carried out almost exclusively by the fluidized-bed process. In the discontinuous fixed-bed process, which is now hardly used, rutile concentrate (> 96%) is mixed with 20–25% petroleum coke and a binder (wood tar, asphalt, etc.), sometimes with added catalysts (e.g., MnO_2), and briquetted [144]. The briquettes are stacked in the lower part of a brick-lined chlorination tower over a layer of carbon which acts as an electrode, and are reacted with chlorine at 500–850 °C. The chlorine gas is heated to ca. 1000 °C by the resistance-

heated carbon bed and then reacts exothermically with the rutile and carbon in the briquettes.

The process can also be carried out in two stages, in the first of which rutile is reduced by carbon at 1200–1400 °C to give titanium carbide and titanium monoxide. The latter reacts with chlorine more readily than rutile.

Since ca. 1950, chlorination has been carried out almost exclusively by the fluidized-bed process because of its higher reaction rate and improved heat transfer, and also because of the shortage of briquetting facilities. Also, higher temperatures (ca. 1000 °C) can be achieved. After the reaction has started at ca. 600 °C no further external heat supply is necessary. Apart from the benefit of continuous operation, fluidized-bed chlorination has the further advantage of being less sensitive to impurities in the rutile or the carbon. The conversion of chlorine is 95–100%, of rutile titanium 90–95%, and of carbon 95%.

Ilmenite is now less often used as starting material, because of excessive chlorine consumption due to formation of iron(III) chloride for which there is little demand and from which chlorine can only be recovered at high cost. Furthermore, in spite of its higher boiling point, FeCl_3 is entrained by the TiCl_4 vapor and is deposited in the coolers as a powder, its solubility in liquid TiCl_4 being only 0.03% [145].

In contrast to the ilmenite-treatment process, the treatment of TiO_2 -rich slags containing < 10% iron is increasing in importance: As these materials contain lower oxides of titanium, they react with chlorine at lower temperatures and require less carbon than rutile [146]. However, compared with rutile, problems are caused by the higher iron content of these slags and their alkaline earth metal content. Calcium and magnesium are converted to their chlorides, which are molten at the reaction temperature and coat the surface of the briquettes in the fixed-bed process, preventing chlorine from penetrating. In the fluidized-bed process, the continuous addition of an inert bed (sand) can give good gas distribution and dilution of the chlorides, so that with continu-

ous removal of residues, slags containing up to 6% calcium or magnesium can be treated.

The use of other reducing or chlorinating agents (CO , COCl_2 , CCl_4 , sulfur chlorides) and other methods of producing TiCl_4 has not achieved industrial importance. For example, the electrolysis of a chloride melt using titanium carbide anodes has been proposed [147]. The most promising process seems to be to digest ilmenite with sulfuric acid and precipitate potassium hexachlorotitanate from the sulfate solution after removal of iron. On heating, this decomposes to form TiCl_4 vapor and KCl , which is returned to the process [148].

Separation and Purification of Titanium Tetrachloride. In the chlorination of rutile, the reaction products are gaseous, consisting of TiCl_4 and CO , with small amounts of CO_2 , phosgene (COCl_2), and other metal chlorides.

The gases leaving the chlorination reactor are cooled by heat exchangers and by spraying with titanium tetrachloride, and the iron(III) chloride that precipitates at 150 °C is scrubbed out by the TiCl_4 [149]. Further cooling causes the titanium tetrachloride to condense. The yellow filtered product contains 94% TiCl_4 , ca. 4% solid constituents such as rutile, carbon, sulfur, and insoluble metallic chlorides, and 2% soluble metal oxide chlorides. The chlorides include SiCl_4 and SnCl_4 (low-boiling substances), VOCl_3 which has a similar boiling point (127 °C) to TiCl_4 (136 °C), and FeCl_3 and AlCl_3 , which have higher boiling points. Other high-boiling chlorides, e.g., of calcium, manganese, magnesium, and sodium, produce unwanted deposits in the equipment.

To purify TiCl_4 (Section 22.7.3.2 and Figure 22.11), the solid constituents are first allowed to settle out. Small amounts of water are added to precipitate aluminum as its oxide chloride. SiCl_4 and SnCl_4 are removed by distillation at < 136 °C. H_2S is passed in and copper powder is added at 90 °C to reduce VOCl_3 to VOCl_2 , which precipitates. FeCl_3 and AlCl_3 distil at > 136 °C. Unsaturated organic compounds, especially oleic acid, promote good

separation of chromium and vanadium oxychlorides [150].

Dissolved chlorine can be removed by simply heating or by heating with metal powders (iron, copper, or tin). Purification with H_2S can also be carried out continuously in a fluidized bed of silica sand or iron sulfide at 140–300 °C. The impurities then form solid products which can be continuously removed from the fluidized bed.

The purified titanium tetrachloride contains only 0.002% V_2O_5 , and is fractionally distilled to remove residual phosgene and SiCl_4 . The purity of the TiCl_4 is 99.9% min.

22.9 Production of Titanium Sponge

The large heat of formation of titanium dioxide (945.4 kJ/mol) combined with the high solubility of oxygen in titanium at high temperatures has so far made it impossible to develop an economic process for the direct reduction of titanium dioxide to low-oxygen titanium metal. The standard industrial processes for the production of titanium metal are therefore based on titanium halides.

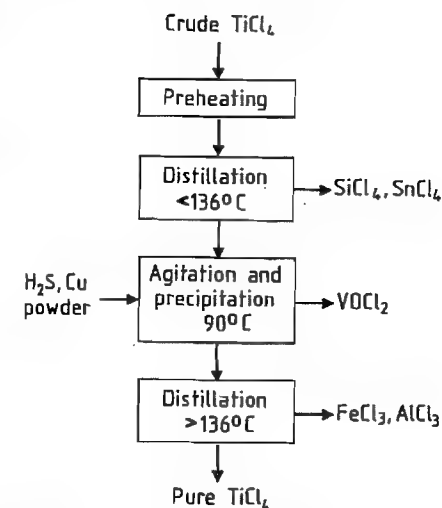


Figure 22.11: Purification of crude titanium tetrachloride.

22.9.1 Reduction of Titanium Dioxide

The reduction of titanium dioxide by carbon is only possible above 6000 °C. Using carbon-containing reducing agents, some titanium carbide is formed, even in high vacuum [151, 152]. Reduction by hydrogen in the presence of inert gases leads to mixtures of lower oxides [153]. A more complete reduction of titanium dioxide is only possible with alkaline earth metals, whereby reduction with calcium gives the lowest oxygen content [154]. Using reactions at temperatures of 600–1200 °C in a vacuum followed by dissolution of excess calcium and calcium oxide in hydrochloric acid, an oxygen content of 0.1–0.3% in the titanium is obtained [155]. Reduction with calcium hydride at 600–700 °C gives titanium hydride, which decomposes at 900 °C into titanium (containing 0.2% oxygen) and hydrogen [156].

22.9.2 Reduction of Titanium Halides

When TiCl_4 is reduced with hydrogen in an electric arc, subchlorides are formed in side reactions, and this reaction is consequently uneconomical on an industrial scale [157]. The reduction of TiCl_4 with calcium is strongly exothermic [158], but this reaction also has not been used commercially.

Reduction of Titanium Tetrachloride with Sodium. In 1910, HUNTER succeeded in producing larger quantities of pure titanium by reacting titanium tetrachloride with sodium in an evacuated steel bomb [159].

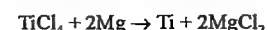
The Degussa process uses a mixture of oxide-free sodium and potassium at 700–800 °C. To prevent overheating (sodium chloride *mp* 797 °C, sodium *bp* 877 °C), molten sodium chloride is first placed in the reactor [160]. Finely powdered sodium chloride at 200–620 °C can also be used. Molten sodium is then fed into the reactor from above, and TiCl_4 is blown in from below, together with the inert gas [161].

In industrial plant molten sodium and TiCl_4 are fed simultaneously into a steel reactor filled with argon, heated to 650 °C. After the reaction has begun, the temperature can rise to 900 °C. When reaction is complete, more sodium is added and the temperature is raised to 950 °C.

In the two-stage process, TiCl_4 is first converted at 235 °C into low-melting sodium titanium chloride compounds and titanium(II) chloride, and is then reduced to titanium and sodium chloride in a second reactor after further addition of sodium. This technique distributes the heat of reaction, and the process is therefore more easily controlled. After size reduction of the reaction product, the NaCl is dissolved in water, and the titanium sponge left behind is centrifuged off and dried.

The Hunter process has been almost completely superseded by the Kroll process. Industrial scale plants are currently only operated in China [162].

Reduction of Titanium Tetrachloride with Magnesium (Kroll Process). The reduction of titanium tetrachloride with magnesium



was discovered by KROLL [158, 163], and was developed into an industrial process by the Bureau of Mines in Boulder City, Nevada [164]. Magnesium boils at 1120 °C, and magnesium chloride melts at 711 °C. The resulting temperature range and the high purity of magnesium are advantageous for the industrial production of titanium sponge from TiCl_4 .

The reactor is constructed of plain carbon steel, chromium–nickel steel, and the interior walls are cleaned by brushing, or are titanium coated. The reactor is charged with oxide-free lumps of magnesium and filled with argon, and the magnesium is melted at 651 °C (Figure 22.12). When the temperature reaches 700 °C, purified TiCl_4 is run in slowly from above or blown in as a vapor, such that a reaction temperature of 850–950 °C is established. The titanium sponge is deposited on the reactor walls and forms a solid cake above the molten magnesium. The molten MgCl_2 collects beneath the magnesium and is drawn off.

The magnesium rises through the porous cake to its surface by capillary action, and reacts there with the gaseous TiCl_4 .

The temperature must not exceed 1025 °C, to prevent reaction between the titanium and the iron of the reactor, although titanium can pick up iron even below 950 °C. The amounts of TiCl_4 reacted are 10–15% substoichiometric amount, as some of magnesium and MgCl_2 remain in the titanium sponge. However, an excess of TiCl_4 leads to the formation of lower titanium chlorides and iron chlorides, which increases the iron content of the titanium sponge.

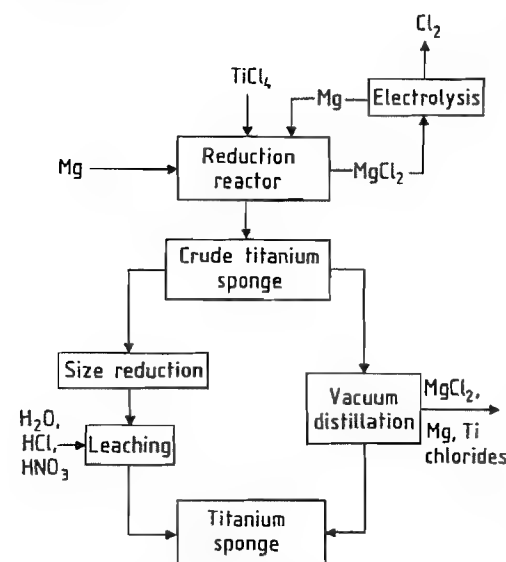


Figure 22.12: Reduction of titanium tetrachloride to titanium sponge by the Kroll process (reduction with magnesium).

The temperature range that can be used in practice is 850–950 °C, the lower temperatures giving longer reaction times but purer titanium sponge. After the molten MgCl_2 has been removed and the temperature of the reactor contents has fallen below 200 °C, the reaction vessel is opened in a dry room (MgCl_2 and titanium chloride are hygroscopic).

The crude titanium sponge is generally purified by vacuum distillation; leaching is now rarely used. Around 98% of titanium sponge produced is vacuum distilled. Immediately af-

ter completion of the reaction a vacuum hood usually is attached to the reduction reactor. At ca. 0.1 Pa (10^{-3} mbar) and 900–1000 °C, the metal chloride impurities, mainly magnesium and titanium chlorides, are distilled off together with magnesium metal while the titanium sponge remains behind.

In the leaching process, the size-reduced sponge is treated with a hot mixture of hydrochloric and nitric acids (8% HCl, 3% HNO₃) in tanks or in an inclined rotating titanium drum containing an Archimedean screw. Because of the heat of solution of the MgCl_2 , cooling must be provided to prevent the temperature from exceeding 25 °C. During leaching, the titanium sponge picks up hydrogen, which can be removed by melting in a vacuum electric-arc furnace with a high-performance vacuum pump.

The process of drilling out the crude sponge from the reactor can be avoided by using a perforated crucible if the level of the molten magnesium is maintained above the perforated base [165]. Removal of the sponge from the perforated crucible can be facilitated by facing it with stainless steel or high-carbon steel sheet.

The reduction reactors, usually gas heated, have titanium sponge capacities between 1.5 and 10 t. Production of 1 kg titanium sponge theoretically requires 3.96 kg TiCl_4 and 1.015 kg magnesium, 3.975 kg MgCl_2 being formed. However, in practice, only 65–70% of the magnesium takes part in the reduction process. Most of the remainder is recovered in vacuum distillation, whereas it is lost in the leaching process. The magnesium is recovered from MgCl_2 electrolytically. The proportion of the titanium sponge that can be used for the production of titanium metal is 75–85%, and the total titanium yield is ca. 98%. The energy consumption is 30 kWh/kg titanium sponge. The reduction process takes ca. 95 h, and the distillation ca. 85 h.

Variants of the Kroll process, so far not used industrially, are aimed at giving better separation of the sponge from the MgCl_2 and at achieving continuous operation. For example, in a ram reactor the sponge is compressed

by a ram and is ejected as compact metal from the magnesium chloride bath [166].

The reduction can be carried out under vacuum instead of in an argon atmosphere, and the magnesium chloride can be distilled off immediately after completion of the reaction [167].

The simultaneous injection of TiCl_4 vapor and magnesium vapor into a reactor packed with titanium netting at 800–1100 °C and ca. 10^{-2} Pa produces pure titanium, which grows as crystals on the netting, while the by-products (Mg vapor and MgCl_2 vapor) distill off [168].

In Japan, a quasi-continuous process is being developed in which the distillation of TiCl_4 , Mg, and MgCl_2 and the melting of a titanium block are performed simultaneously [169]. A production of ≥ 500 t titanium sponge per furnace per month is expected.

Comparison of the Sodium and Magnesium Reduction Processes. Both methods are used industrially and produce titanium sponge of sufficiently high purity. Their advantages and disadvantages are as follows:

Sodium has a lower melting point than magnesium and can therefore be transported in the molten state. Reduction with sodium requires only the theoretical quantity, whereas ca. 130% of the stoichiometric quantity of magnesium is required. With sodium reduction, the titanium sponge is more easily removed from the reactor, as NaCl collects on the reactor walls, while in the Kroll process the sponge builds up on the reactor walls. Sodium chloride is soluble in water and is therefore easily removed from the titanium sponge. This is a more economic method than vacuum purification of the titanium sponge produced by magnesium reduction. The density of magnesium-reduced sponge is 1.0–1.2 g/cm³, (sodium-reduced sponge 0.7–0.9 g/cm³) and it has larger particles than sodium-reduced sponge, which contains a high proportion of fines. Typical figures for the chemical composition of various types of sponge produced by both processes are listed in Table 22.16. This titanium from the Kroll process has a lower

average oxygen content and that from the sodium reduction process, a lower average iron content. The highest purity achieved in the Kroll process so far is reported to be 99.999% [169].

The costs of reduction with sodium are usually ca. 10% lower than reduction with magnesium, although the economics of the Kroll process can be improved by using larger reduction reactors, improved vacuum distillation, and higher capacity electrolysis cells for recovery of magnesium. In both cases, batch operation is a disadvantage.

The sponges produced by different processes of chemical reduction, size reduction, and purification differ in hardness, lump size, density, and compressibility, but all are equally suitable for melting into ingots. Therefore, the reasons for selecting a particular reduction process are mainly economic, e.g., availability and reprocessing of reduction metals, energy costs, and capital costs.

In 1995, ca. 98% of world titanium-sponge production was by the Kroll process.

Reduction of Titanium Tetrafluoride. Titanium tetrafluoride is easily produced from titanium dioxide and hydrogen fluoride, can be readily purified by sublimation, and, in contrast to titanium tetrachloride, titanium tetrafluoride can also be reduced by silicon. The high-purity titanium so produced contains only 0.009% silicon [170].

22.9.3 Thermal Decomposition of Titanium Halides

The oldest process of this type is that of VAN ARKEL and DE BOER in which titanium tetraiodide is decomposed on electrically heated tungsten wires at 1000 °C. If wires or single crystal fibers of titanium are used, tungsten-free titanium of the highest purity can be obtained (as a single crystal in the latter case). The iodine liberated is reacted with crude titanium to regenerate titanium tetraiodide in the same vessel below 200 °C or above 500 °C. Above 200 °C lower titanium iodides (TiI_2 , TiI_3) are formed, which only act as titanium

carriers above 500 °C because of their low volatility [171]. The process enables titanium of the highest purity to be produced from crude titanium or titanium scrap.

Very high purity titanium can also be obtained by thermal disproportionation of titanium(II) chloride or bromide. By passing TiCl_4 vapor over titanium-containing material (titanium scrap, crude titanium, or titanium alloys) at 950–1500 °C, TiCl_2 vapor is formed, which condenses and is decomposed at ca. 1000 °C



The TiCl_4 is fed back to the process [172].

22.9.4 Electrowinning of Titanium

The high affinity of titanium for oxygen and hydrogen together with its electrode potential ($\text{Ti}/\text{Ti}^{2+} = -1.75$ V) prevents its deposition from aqueous solution [173]. Hence only molten salt electrolysis can be used.

Titanium dioxide is almost insoluble (0.07–0.02%) in molten chlorides of alkali metals and alkaline earth metals. It is soluble (ca. 8%) in sodium and potassium fluorides and in potassium hexafluorotitanate (ca. 14%) [174]. However, attempts to electrolyze the oxide in halide melts (in analogy to aluminum production) only produced lower titanium oxides [175]. Thus only titanium halides are suitable starting materials for molten salt electrolysis.

Titanium tetrafluoride combines with alkali metal and alkaline earth metal fluorides to form complex hexafluorotitanates. These compounds decompose below their melting

points with vaporization of titanium tetrafluoride. They can only be used in molten salt electrolysis as components of a low-melting molten salt bath containing other diluent salts [176]. Special problems arise in molten salt electrolysis with graphite electrodes due to the anode effect. Although this can be counteracted by controlled addition of oxides to the salt bath, oxygen pickup by the titanium metal produced must be prevented by using low temperatures, by separating the anode space from the cathode space, and by avoiding turbulence in the electrolyte [177].

Although **titanium tetrachloride** is insoluble in molten alkali and alkaline earth metal chlorides, stable molten electrolytes can be obtained by using lower titanium chlorides. These can be produced directly from titanium tetrachloride in the electrolytic cell, but they react with the chlorine liberated at the anode to reform titanium tetrachloride, which then evaporates. This can be avoided by using a porous, basket-shaped cathode into which the titanium tetrachloride is fed, as the electrolyte (e.g., an NaCl– SrCl_2 eutectic) can then be kept free of lower titanium chlorides [178, 179].

The problems of electrolyte composition and the anode effect can be completely solved by using soluble anodes, as in this case no changes to the electrolyte occur and no gas is emitted at the anode, at least at low current densities [180]. Soluble anodes can be made of crude titanium, titanium scrap, and titanium compounds such as titanium carbide, sometimes mixed with titanium monoxide [181, 182] and titanium nitride [183], which can be produced directly from titanium ores.

Table 22.16: Chemical composition (in %) of titanium sponge.

Reduction process	Maximum hardness (Brinell)	C	N	O	H	Fe	Mg	Na	Cl
Magnesium	95	0.006	0.003	0.045	0.002	0.02	0.03		0.10
	100	0.08	0.05	0.5	0.002	0.04			0.09
	110	0.08	0.05	0.6	0.002	0.05	0.03		0.08
	120	0.08	0.05	0.7	0.002	0.06	0.03		0.09
Sodium	120	0.009	0.004	0.07	0.01	0.016		0.08	0.13
Electrolysis	60	0.003	0.002	0.01	0.003	0.001			0.08
	75	0.013	0.004	0.03	0.004	0.0040.0			0.09
	90	0.018	0.004	0.04	0.004	20			0.16

Semitechnical plants using processes analogous to the production of magnesium from magnesium chloride can operate at 900 °C under argon, using TiCl_4 and NaCl as starting materials. The NaCl fed into the cathode space is decomposed, and the sodium liberated reduces the TiCl_4 (which is fed in later) stepwise via TiCl_3 , TiCl_2 , and TiCl to give titanium. The energy consumption is only 40% of that required for the reduction of TiCl_4 with magnesium (ca. 43 kWh/kg) [184].

All electrolytic processes yield a very pure metal (> 99% titanium), but have the disadvantage that the titanium is produced at the cathode in the form of poorly adhering dendritic crystals. The cathodes must be lifted out of the molten electrolyte and cooled in an inert atmosphere. The titanium metal is then scraped off and removed from the electrolytic cell through an air lock.

A production plant, now shut down, to produce titanium sponge electrolytically operated at 520–650 °C with an electrolyte consisting of a mixture of LiCl and KCl of approximately eutectic composition and with TiCl_4 as the raw material. The titanium concentration in the electrolyte is ca. 1.5%. The TiCl_4 is fed through a steel tube into the molten electrolyte in a metal crucible. The graphite anode is surrounded by a wire mesh coated with cobalt or nickel. Metallic titanium is deposited on steel cathodes. After size reduction, dissolution of the salt in 0.5% hydrochloric acid, washing, and drying, the titanium yield is ca. 98% [185].

A number of attempts have been made to produce titanium by electrolytic processes on an industrial scale but none have led to permanent application [162].

22.10 Processing and Reuse of Scrap Metal

With increasing titanium production, the use of titanium scrap as a raw material instead of titanium sponge has become increasingly important. Titanium scrap is produced during the production of semifinished products, their

processing to finished products, and the scrapping of used equipment. Before remelting, titanium scrap must be pretreated. Adhering scale and other residues must be removed from the surface by abrasive blasting, pickling, or surface grinding. The various alloys must be sorted so that the alloy added to the melt is of consistent quality. Depending on the melting process, the scrap may be mixed with the sponge and compressed, or may be welded together for addition in the form of a consumable electrode. Alternatively, it can be directly added to the melt in small pieces. In another process, ground, hydrogenated titanium scrap is used instead of titanium sponge for melting to obtain titanium.

Untreated titanium scrap is used as an additive to steel, nickel, aluminum, copper, and zinc alloys, and in the production of master alloys such as ferrotitanium.

In the United States, ca. 40% of titanium consumption is from processed titanium scrap. In Europe, due to the low price of titanium sponge only 10–30% is accounted for by scrap [186, 187].

22.11 Processing of Titanium Sponge

Melting Processes. Titanium reacts in the molten state with air and with all the conventional crucible materials. Melting is therefore only possible under vacuum or in an inert gas atmosphere in cooled metal crucibles of high thermal conductivity, usually copper. The crucible walls are cooled with water or molten sodium–potassium alloy. The energy source is chiefly an electric arc, although to an increasing extent the metal is melted by a plasma, by electron beams, or, on the laboratory scale, by induction.

On the industrial scale, vacuum arc furnaces are generally used, with consumable electrodes made of titanium sponge, titanium scrap, and alloy components. Vacuum arc furnaces with rotating water-cooled copper electrodes are only used for first stage melting.

To produce consumable electrodes, titanium sponge, sometimes mixed with scrap and alloying components, is compressed to form electrode pieces, which are welded into electrodes, by plasma or MIG welding. Large pieces of scrap can also be welded together to form electrodes.

The melting of the electrode (negative pole) takes place when the arc is formed with the bottom of the crucible under argon or a vacuum of ca. 1 Pa (10^{-2} mbar), with currents of 15–40 kA and an average melting capacity of 1 kg/kWh. The solidified titanium is remelted in a similar manner, as this gives improved homogeneity. For special applications involving critical service conditions, the titanium is melted three times.

Vacuum arc with solid negative electrodes [188] and cold-hearth melting furnaces with electron-beam (EBCHM) [189] or plasma heating (PCHM) [190] do not require consumable electrodes. The sponge and scrap in lump form are melted by feeding them continuously into the molten metal. These furnaces have so far only been used for the first melt. In cold-hearth melting, sponge and processed scrap are melted in a pre-crucible. The melt is fed into the mold through a channel, whereby impurities can be retained in the skull—the solidified surface forming on the melt in the channel. This method is expected to give better retention of impurities from the scrap. The mold can be designed for producing ingots or slabs. Multiple burners are employed to obtain a continuous ingot or slab. The crucible is equipped with a withdrawable bottom, and the crude ingot is melted to form a strand which is lowered at a rate corresponding to the melting process.

The commercial crude ingots produced by melting can have a mass of 1–13 t, but are usually in the range 3–8 t. Diameters are in the range 500–1100 mm.

Casting. When arc furnaces with consumable or solid electrodes are used [191], the titanium

drains into water-cooled tilting copper crucibles, or the melt is superheated by electric current under an inert gas. The metal is cast in graphite, ceramic, or metallic molds, or by centrifugal casting. Electron-beam furnaces can also be used [192]. Depending on the process, the mass of a casting can range from 750 kg to a few grams in the case of high precision castings with small wall thicknesses produced by the lost wax process. The output of titanium castings is barely 1% of the total output of semifinished products. In a new melting process a combination of cold-wall crucible and plasma burner is used.

Powder Metallurgy. The production of components from titanium and titanium alloys by powder metallurgy has so far not achieved industrial importance. Production of powder by sieving the fine material from titanium sponge or by supersaturating the sponge with hydrogen, milling under inert gas, and dehydrogenation [193] are not widely used because of the poor flow properties of the powder obtained. These properties can be improved by partial melting of the powder to give spheroidal particles.

Spheroidal powder with good flow properties and good densification behavior can also be produced by an atomization process in which titanium rods are rotated at high speed in an electric arc or plasma [194].

Advances in cold-wall crucible technology have now made possible inert gas atomization with argon or helium in a ceramic-free process [195]. Fine, spheroidal titanium powder can be produced by the induction drip-melting atomization process and by the electrode-induction-melting, gas-atomization process.

In the calciothermic production of titanium alloys in powder form, the starting materials are the metal oxides, CaO, Ca, and KClO_4 . Fine powders with good densification properties (60%) and with oxygen contents of 0.14–0.18% and carbon contents of 0.03–0.06% [196] are obtained.

22.12 Production and Processing of Semifinished Products

Semifinished products are chiefly produced by pressing, forging, rolling, or drawing.

Hot Forming. In hot forming, the temperature of the metal is above its recrystallization temperature. A slightly oxidizing atmosphere and a uniform temperature are maintained in the reheating furnace to prevent hydrogen pickup and consequent embrittlement. In hot rolling, temperatures are usually 20–100 °C below those used for forging.

For pressing or forging heavy section components, a preforming stage is carried out in the β -range, and the final is then carried out, usually in the $(\alpha + \beta)$ -range sufficiently below the $(\alpha + \beta)/\beta$ -interphase, with deformations of at least 60–75% to produce the desired structure and properties of the material.

Cold Forming. In cold forming to produce wire, thin sheet, and foil, the high yield strength of titanium, which increases with increasing tensile strength, and the low elongation without necking must be taken into consideration. Commercially pure titanium should be work annealed after 30–40% deformation.

Heat Treatment after Deformation. Low-strength titanium (Grade 1, DIN designation 3.7025) generally does not require stress-relief annealing, but annealing is necessary for higher strength and especially complex components.

Recrystallization annealing to give a ductile product is required after hot forming of semifinished and drop forged products, and for work annealing after forming of sheet.

Descaling and Pickling. Titanium is descaled by abrasive blasting followed by pickling in aqueous mixtures of 20–40% HNO_3 and 1–3% HF , in sodium hydroxide-based salt baths with added oxidizing agents such as sodium nitrate and borax at 450–510 °C, or in sodium

hydride baths at 380 °C. Hydrogen pickup can occur if the pickling time is too long.

Processing of Semifinished Products. Of the noncutting forming processes, deep drawing can be used with titanium-based materials, but stretch-forming is less suitable. In cutting, stamping, pressing, and hole punching, titanium behaves like steel. To give crack-free bending, folding, and edging, radii should be large and deformation rates small. The use of load-bearing lubricants and plastic coatings gives improved drawing behavior [197].

In machining, the low thermal conductivity, low specific heat capacity, low modulus of elasticity, and high toughness lead to considerably higher temperatures in the contact zone than with steel under similar cutting conditions. Also, because of the small extent of chip compression, the contact zone is restricted, leading to additional thermal stress on the tip of the tool. For low heat generation at the tool a high cutting speed, a low chip removed rate, and sufficient cooling should be provided.

Chemical and electrochemical machining of mechanically machined surfaces are widely used processes, and give high accuracy. Hydrofluoric acid, usually with additions of nitric or chromic acid, is used for chemical machining, while electrochemical machining is carried out with direct current in a solution of NaCl .

Welding. In principle, titanium of all strength grades is weldable. However, it can only be welded with exclusion of air or in an inert gas atmosphere because hot solid or molten titanium reacts readily with the atmosphere, reducing toughness and causing embrittlement, even with low levels of pickup. Electron-beam welding is limited to special applications, particularly the aerospace industries, but MIG, TIG, plasma, and laser-beam welding are widely used. Friction and diffusion welding can also be employed with titanium.

Soldering is only possible if a solderable coating is first applied to titanium. For brazing, the dense passive layer on the titanium must first be removed by a flux, which usually consists

of alkali metal halides with addition of AgCl . Suitable solders include silver, titanium–silver, and aluminum–silver alloys. It is preferable to solder in a vacuum or in an inert gas atmosphere to minimize diffusion of atmospheric gases into the metal [198]. Soldered joints can have a tensile strength of $> 800 \text{ N/mm}^2$ and a shear strength of ca. 150 N/mm^2 .

Adhesives. Adhesive bonds with shear strengths of $> 200 \text{ N/mm}^2$ can be produced if the titanium surface is pretreated and anodically oxidized or coated with metals by spraying or vapor deposition [199, 200].

Explosive Cladding. Industrial low-strength grades of titanium can be applied to metallic substrates, usually steel, by explosive cladding at ca. 5000 MPa, giving shear strengths of ca. 300 N/mm^2 . To prevent diffusion between the parent metal and the coating leading to embrittlement of the bonding zone, the upper limit of the usage temperature should be 550 °C [201]. Other substrate metals such as aluminum, copper, and zirconium can also be explosively clad.

Super Plastic Forming (SPF). Alloyed titanium with a two-phase fine structure often exhibits ductility properties that allow ca. 1000% elongation. In combination with diffusion welding, highly complex structural components can be produced in a single operation [202].

Tribology. In general, the surface of titanium components is not very resistant against wear. Therefore, wear resistant films are formed by ion implantation or by PVD or CVD. In-situ formation of titanium nitride, carbide, or boride films of varying thickness is achieved by annealing under the corresponding atmosphere or by laser melting [203–207].

22.13 Compounds [208, 209]

Titanium is usually quadrivalent in its compounds, but may also function as trivalent and,

in a few compounds as bivalent; the compounds of bivalent titanium are prepared only with difficulty, and are unstable in aqueous solution. The existence of titanium(I) compounds has not been established, although certain observations point to their formation, e.g., the observation that there is a maximum volatility in the Ti–S system at a composition corresponding roughly to the formula Ti_2S .

Quadrivalent titanium has a strong tendency to form anions such as $[\text{TiO}_3]^{2-}$ (titanate ion), $[\text{TiF}_6]^{2-}$ (fluorotitanate ion), $[\text{TiCl}_6]^{2-}$ (chlorotitanate ion), and $[\text{Ti}(\text{SO}_4)_3]^{2-}$ (sulfatotitanate ion). The soluble titanium(IV) compounds have a strong tendency to undergo hydrolytic decomposition. Incomplete hydrolysis may give rise to compounds of the type TiOx_2 . Compounds containing the radical $[\text{TiO}]^{2+}$ are called titanyl compounds.

The oxidation potential $\text{Ti}^{3+}/\text{Ti}^{4+}$ (referred to the normal hydrogen electrode at 0 °C) is +0.04 V. If a platinum foil is dipped in a solution containing equal concentrations of Ti^{3+} and Ti^{4+} ions, and combined with a normal hydrogen electrode to form a galvanic cell, the current flows through the wire joining the two electrodes from the normal hydrogen electrode to the platinum foil dipping in the titanium salt solution. Hydrogen is evolved at the former, while Ti^{3+} ions are oxidized to Ti^{4+} ions at the latter. Titanium(III) ions have so strong a reducing action, that in some circumstances they can evolve hydrogen from acid solutions. For the couple $\text{Ti}^{2+}/\text{Ti}^{3+}$ the oxidation potential $E^0 = +0.37 \text{ V}$, for the couple $\text{Ti}^{2+}/\text{Ti}^{4+}$, $E^0 = +0.20 \text{ V}$. The normal potential of Ti in contact with a Ti(II) salt solution is +1.75 V.

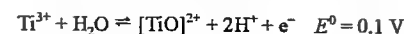
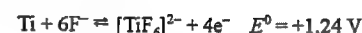


Table 22.17 gives a summary of the most important titanium compounds.

Table 22.17: Titanium compounds.

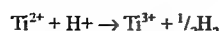
Type	Compounds	Color
Fluorides	TiF ₃	violet
	TiF ₄	white
Chlorides	TiCl ₂	black
	TiCl ₃	violet
	TiCl ₄	violet
Bromides	TiBr ₂	black
	TiBr ₃	black
	TiBr ₄	amber
Iodides	TiI ₂	black-brown
	TiI ₃	dark violet
	TiI ₄	red-brown
Oxides	TiO	gold
	Ti ₂ O ₃	violet
	Ti ₄ O ₇ (?)	dark blue
	TiO ₂	white
Sulfides	TiS _{<1}	grey
	TiS	dark brown
	Ti ₂ S ₃	green-black
	TiS ₂	brassy
	TiS ₃	graphite-like
Phosphides	Ti ₃ P (?)	
	TiP	
Carbides	Ti ₂ C (?)	
	TiC	black
Nitrides	TiN	gold

22.13.1 Titanium(II) Compounds

Compounds of bivalent titanium can be prepared by reduction of titanium(IV) or titanium(III) compounds. Thus titanium(II) chloride, TiCl₂, is produced from titanium tetrachloride by means of sodium amalgam, as a black powder which is slowly decomposed by water with the evolution of hydrogen. Aqueous solutions which contain titanium(II) chloride (together with titanium(III) chloride) can be prepared by dissolving TiO in cold dilute hydrochloric acid. Ti²⁺ ions are rapidly oxidized to Ti³⁺ ions by water at ordinary temperature; the solutions are more stable at lower temperatures. In the pure state, TiCl₂ (*d* 3.13) is best obtained, by thermal decomposition of TiCl₃, or by heating TiCl₄ with Ti shavings. TiBr₂ (*d* 4.31) and TiI₂ (*d* 4.99) can be prepared by direct union of their components.

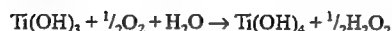
TiO (*d* 4.94, *mp* 175 °C) can be obtained by heating a mixture of TiO₂ and Ti. It has the NaCl type crystal structure, but a certain proportion of the lattice sites (distributed at ran-

dom) is vacant. At the one end of the homogeneity range, these vacant sites represent missing Ti atoms, and at the other extreme O atoms. When TiO is dissolved in dilute hydrochloric acid, partial oxidation occurs:



22.13.2 Titanium(III) Compounds

Titanium(III) compounds are obtained by reducing soluble titanium(IV) compounds with zinc and acid, or electrolytically. The solutions contain violet colored titanium(III) ions; these have a strong tendency to revert to titanium(IV) ions. The ability of trivalent titanium to bring about indirect oxidation by means of oxygen is so great that even water can play the part of an acceptor in the presence of titanium(III) compounds in alkaline solution, and is thereby converted to hydrogen peroxide:



Anhydrous titanium(III) chloride is obtained as a violet powder by passing the vapor of titanium tetrachloride, mixed with excess hydrogen, through a red hot tube. When it is heated in hydrogen to about 700 °C it decomposes into TiCl₂ and TiCl₄. Titanium(III) chloride is obtained in solution by reducing a solution of titanium(IV) salt in hydrochloric acid by means of zinc, or by dissolving metallic titanium in hydrochloric acid. A violet hexahydrate, TiCl₃·6H₂O, crystallizes from the solution.

TiBr₃·6H₂O forms reddish violet crystals (*mp* 115 °C) which are readily soluble in alcohol and acetone, as well as in water. Anhydrous TiBr₃ exists in two modifications. It decomposes reversibly at 400 °C, according to:



TiF₃ may be obtained as a dark blue powder by treating Ti or TiCl₃ with HF. It is very unreactive chemically, and begins to sublime at 900 °C in a vacuum.

22.13.2.1 Titanium(III) Sulfate and Double Sulfates

In the electrolytic reduction of a sulfuric acid solution of titanium(IV) sulfate, a black-violet colored solution is first obtained. The solution becomes lighter with continued reduction, and when practically all the titanium is converted to the trivalent state, it has a transparent pure violet color. An acid titanium(III) sulfate, with the composition 3Ti₂(SO₄)₃·H₂SO₄·25H₂O can be isolated from the solution in the form of a crystalline violet powder. This may be converted to anhydrous neutral titanium(III) sulfate, Ti₂(SO₄)₃, by fuming with sulfuric acid.

Neutral titanium(III) sulfate is a green crystalline powder, insoluble in water but soluble in dilute acid giving violet solutions. Exchange of hydrogen in acid titanium(III) sulfate by metal ions gives rise to double or complex salts, with the composition 3Ti₂(SO₄)₃·M₂SO₄, or M^ITi₃(SO₄)₅, (with variable water content), e.g., an ammonium salt NH₄Ti₃(SO₄)₅·9H₂O, forming blue crystals, sparingly soluble in water. Another type of double sulfate of trivalent titanium corresponds to the alums in composition and crystalline form. The only known titanium alums are the rubidium and cesium compounds, e.g., RbTi(SO₄)₂·12H₂O (red-violet). These salts can be recrystallized without decomposition from dilute sulfuric acid, but not from water. Yet another type is represented by the sodium double sulfate, a violet crystalline mass with the composition NaTi(SO₄)₂·2.5H₂O.

22.13.2.2 Titanium(III) Hydroxide

Formed by reaction of titanium(III) salt solutions with alkali hydroxides, as a deeply colored precipitate which acts as a vigorous reducing agent, and is therefore difficult to obtain pure.

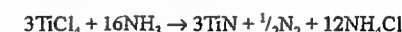
22.13.2.3 Titanium(III) Oxide

Dititanium trioxide, Ti₂O₃ (*d* 4.49, *mp* about 1900 °C), may be obtained crystalline

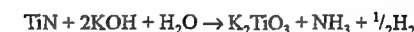
by heating titanium dioxide at 1000 °C in a stream of hydrogen and titanium tetrachloride. It has the same crystal structure as corundum.

22.13.2.4 Titanium Nitride, TiN

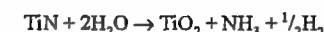
If titanium compounds are reduced at high temperature in the presence of nitrogen, titanium nitride is readily formed in an impure state. Pure titanium nitride TiN is obtainable in the form of a bronze colored powder by strongly heating titanium tetrachloride in a current of ammonia:



It has a structure of rock salt type, decomposed by hot caustic potash:

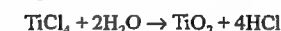


and by superheated steam:



22.13.3 Titanium(IV) Compounds

Titanium tetrachloride, TiCl₄, may be obtained by passing chlorine over heated titanium, titanium carbide, or over a mixture of titanium dioxide and carbon. In the pure state, it forms a colorless liquid, boiling at 136.5 °C, solidifying at -23 °C, and having a density of 1.76 at 0 °C. It has a pungent smell, fumes strongly in moist air, and rapidly hydrolyzed by water:

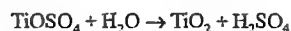


If the hydrolysis is repressed by addition of acid, or if only a little water enters into reaction, oxychlorides can appear as intermediate products. Titanium tetrachloride adds on chloride ions, forming the complex chlorotitanate ion [TiCl₆]²⁻, e.g., the ammonium salt (NH₄)₂[TiCl₆]·2H₂O (yellow crystals). The corresponding free acid can only exist in aqueous solution; its formation therein is demonstrated by the yellow coloration produced by the addition of concentrated hydrochloric acid to titanium tetrachloride.

Titanium fluoride, TiF₄, is prepared by reaction of TiCl₄ with HF, forms a white, powder of density 2.80. It displays a much stronger

tendency than does the chloride to form acid salts. These correspond to the type $M_2^{II}[\text{TiF}_6]$ fluorotitanates. All the alkali and alkaline earth salts of this type, and numerous salts of the heavy metals have been prepared. Titanium tetrabromide, TiBr_4 , obtained in a similar manner to TiCl_4 (as yellow octahedral crystals, d 3.25, mp 40 °C, bp 230 °C), is similar to the chloride in its chemical behavior. It is extremely hygroscopic, soluble in alcohol and moderately soluble in ether. Titanium tetraiodide, TiI_4 , is prepared by double decomposition of TiCl_4 with HI . It crystallizes in red-brown octahedra (mp 150 °C, bp 365 °C).

When titanium dioxide is fumed with concentrated sulfuric acid, titanyl sulfate, TiOSO_4 , is formed, as a white powder, soluble in cold water. It is decomposed by hot water, with the deposition of gelatinous titanium dioxide:



In addition to titanyl sulfate, there are other titanium sulfates, both with greater and with smaller SO_3 contents. The neutral titanium sulfate, $\text{Ti}(\text{SO}_4)_2$, is not known with certainty in the free state. Double salts derived from it are known; in particular the sulfatotitanates of the type $M_2^{II}[\text{Ti}(\text{SO}_4)_3]$. Titanyl sulfate also forms double salts, e.g., $(\text{NH}_4)_2[\text{TiO}(\text{SO}_4)_2] \cdot \text{H}_2\text{O}$.

22.13.3.1 Titanates

Neglecting their water of crystallization, the alkali titanates correspond mostly to the formulas $M_2^{II}\text{TiO}_3$ and $M_2^{II}\text{Ti}_2\text{O}_5$. They may be obtained in the wet way, by evaporating solutions of α -titanic acid in concentrated alkali hydroxide solutions (β -titanic acid is insoluble). They can be prepared in the anhydrous state by fusing titanium dioxide with alkali carbonates. The titanates of other metals can also be prepared by high temperature methods. Compounds of the type $M_2^{II}\text{TiO}_4$ (orthotitanates) are formed in this way by a few metals, as well as those of the type $M_2^{II}\text{TiO}_3$ (metatitanates). Numerous polytitanates (compounds with more than one TiO_2 per one

M_2^{II}O) have been obtained by fusion methods. Alkaline earth titanates are known corresponding to the types $M^{II}\text{TiO}_3$, $M^{II}\text{TiO}_4$, and $M^{II}\text{Ti}_2\text{O}_5$. Calcium titanate, CaTiO_3 , occurs in nature as perovskite. The compound Li_2TiO_3 is not a titanate, but is a double oxide with the rock salt structure.

The more commonly occurring mineral ilmenite, iron(II) titanate, FeTiO_3 , usually contains more iron than is required by this formula. It is isomorphous with hematite, Fe_2O_3 ; in consequence hematite ores often contain considerable amounts of titanium dioxide. The crystal structure of ilmenite is derived from that of corundum, with which hematite is isomorphous, in such a way that the aluminum atoms are replaced alternately by titanium and iron atoms. The metatitanates of Co^{II} , Ni^{II} , Mn^{II} , Cd , and Mg likewise crystallize with the ilmenite structure. CaTiO_3 , SrTiO_3 , and BaTiO_3 , on the other hand, crystallize in the perovskite structure. In the ilmenite structure, as also in the perovskite structure, Ti has the coordination number 6 towards oxygen. The same is true for the structure of the compound Fe_2TiO_5 (crystallizing rhombic), which occurs in nature as pseudobrookite. It is built up of (somewhat distorted) TiO_6 octahedra, which are linked together by two opposite corners, so as to form chains running parallel to the c axis. The iron atoms are inserted into the spaces of the crystal lattice in such a way that every iron atom is surrounded, roughly tetrahedrally, by 4 O atoms. Those titanates of the formula $M^{II}\text{TiO}_4$ for which the structures are known ($M^{II} = \text{Mg}, \text{Zn}, \text{Mn}, \text{Co}$), crystallize with the spinel structure.

Titanite or sphene, a monoclinic mineral of the composition $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$, is best represented by the formula $\text{Ca}(\text{Ti}^{IV}, \text{Fe}^{III})(\text{O}, \text{OH})[\text{SiO}_4]$. X-ray structure analysis has shown that titanite is a silicate built up of isolated, somewhat distorted $[\text{SiO}_4]$ tetrahedra, in the structure of which the Ti atoms are arranged in such a way that each of them is surrounded by the vertices of 4 $[\text{SiO}_4]$ tetrahedra, and also by 20 atoms which link pairs of neighboring Ti atoms together. The Ti atoms can be partially replaced by Fe^{III} . A corresponding proportion

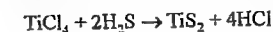
of the O atoms linking them together are then exchanged for OH groups.

22.13.3.2 Peroxytitanic Acid and Peroxytitanates

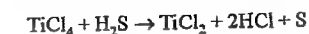
Titanium salts, in neutral or acid solution, are colored an intense orange red by hydrogen peroxide. From sufficiently concentrated solutions, peroxytitanic acid, H_4TiO_5 , can be precipitated by ammonia as a brownish yellow precipitate. Like titanic acid, peroxytitanic acid forms a gel with a variable water content. The compound contains one peroxy group $-\text{O}-\text{O}-$. It was shown to be a true peroxyacid, and not an H_2O_2 -addition product. Peroxytitanyl ions are formed when any dilute, strongly acidified titanium or titanyl salt solutions are treated with hydrogen peroxide. This is made use of for the analytical detection of titanium.

22.13.3.3 Titanium Sulfides

Titanium disulfide, TiS_2 , is formed by passing a mixture of titanium tetrachloride and hydrogen sulfide through a red-hot porcelain tube:



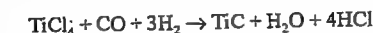
A different reaction takes place between titanium tetrachloride and hydrogen sulfide in the cold, since the latter then acts as a reducing agent, according to:



Titanium disulfide forms brassy-yellow scales, with a metallic luster. It is stable in air at ordinary temperature. When heated it is converted into TiO_2 , and on heating in a stream of hydrogen or of nitrogen it yields lower sulfides, Ti_2S_3 and TiS . It is not decomposed by water even on boiling and is likewise stable towards dilute sulfuric acid, hydrochloric acid, and ammonia. It is decomposed by nitric acid, as well as by hot concentrated sulfuric acid, with the deposition of sulfur. The disulfide is dissolved by boiling caustic potash, with the formation of potassium titanate and potassium sulfide.

22.13.3.4 Titanium Carbides and Carbonitrides

Titanium carbide, TiC , is present in titanium-ferrous cast iron. It was first prepared pure in an electric furnace by Moissan. Small amounts can be obtained by the reaction



taking place on a heated wire, or on the heating of a carbon filament in TiCl_4 vapor. For the preparation of larger quantities of the pure carbide in the compact form, an intimate mixture of finely powdered Ti or TiO_2 and carbon black is first heated in a graphite tube furnace, in an atmosphere of hydrogen, to about 2000 °C. The carbide so formed, after powdering, is compressed under high pressures (2000 kg/cm²) into rods (pellets) and fired in a graphite tube furnace at 2500–3000 °C. The firing process is repeated, after fresh powdering and pressing, until the rod is sufficiently compacted and solidified. This is followed by a high temperature sintering process, in which a powerful electric current is passed through the rod, i.e., it is heated up almost to the melting point of the carbide, whereby the impurities evaporate.

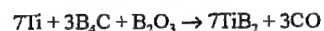
Titanium carbide is similar to titanium metal in appearance and behavior, although less readily attacked by acids, melting point 3450 °C. One g mole of TiC is capable of taking up to about 0.1 g atom of Ti in solid solution. The possible existence of a second carbide, Ti_2C , is uncertain. On account of its great hardness, TiC finds application for the preparation of sintered "hard metals".

Two compounds of titanium with carbon and nitrogen are known: titanium dicyanide (titanium carbonitride, cochraneite), $\text{Ti}(\text{CN})_2$, blue crystals, harder than steel, and titanium cyanonitride, $\text{Ti}_{10}\text{C}_2\text{N}_8$ or $\text{Ti}(\text{CN})_2 \cdot 3\text{Ti}_3\text{N}_2$, red crystals.

22.13.3.5 Titanium Borides

Titanium can take considerable amounts of boron into solid solution. It also forms two compounds with boron: TiB (cubic) crystallizes with the zinc blende structure, and TiB_2

(hexagonal) is isotypic with AlB_2 . TiB_2 is harder than any other known metallic boride. It is prepared technically from boron carbide, B_4C , which is manufactured on a considerable scale as an abrasive. This is mixed with B_2O_3 , and treated with metallic Ti:



22.14 Toxicology and Occupational Health

Ti metal generally shows relatively low toxicity as compared to most other heavy metals. The toxicity of its compounds varies to a large extent, being dependent on their physicochemical properties (e.g., water solubility) and chemical reactivity. Ti apparently is not an essential element for humans [210].

The most important compound of Ti industrially is titanium dioxide, TiO_2 . Titanium tetrachloride is a starting material for other Ti compounds.

In medicine, Ti metal is used in surgical implants and is mostly tolerated by tissue. Other Ti compounds, such as the dioxide, salicylate, and tannate, are widely used in pharmaceutical and cosmetic products. They have been reported to show practically no adverse effects. Ionic cyclopentadienyltitanium(IV) derivatives (titanocene complexes), a new type of antitumor agent, have shown antitumor activities against certain experimental animal tumors [211, 212].

Intoxications with Ti and its compounds are comparatively rare; they occur almost exclusively by occupational exposure.

Biochemistry, toxicokinetics, human and animal toxicity, levels of tolerance, evaluation of health risks to humans, and ecotoxicity of Ti and its compounds have been reviewed [210, 213].

Toxicokinetics. The average intake of TiO_2 in humans is 0.3–0.5 mg/d. Approximately the same amount is excreted daily: at least 0.29 mg/d via the feces and 0.01 mg/d via the urine [210, 214, 215]. The rate of gastrointestinal absorption is about 3% of the ingested mate-

rial, i.e., most of the ingested Ti is excreted unabsorbed. The mean Ti concentration in blood is 0.07 mg/L [216].

The lungs and the lymph nodes are the predominant target organs for the accumulation of TiO_2 [216, 217]. About 0.4 μg Ti is stored in the lungs per day. In experimental studies in rats, after a single exposure to TiO_2 , 40–45% of the deposited material is removed by pulmonary clearance after 25 d. Storage of Ti in the lung is a dose-dependent process [218].

The biological half-life of Ti is between 320 and 640 d. Excretion by other routes than via urine is unknown [210].

Acute Toxicity. Generally TiO_2 behaves as an inert substance which is practically free of acute toxicity. After short-term exposure of guinea pigs to TiO_2 aerosols, an inflammatory response could not be detected; the number of leukocytes and macrophages did not change [219]. In addition, TiO_2 did not lead to the production of hydroxyproline by fibroblasts, which indicates a lack of fibrogenicity [220].

In contrast, TiCl_4 represents a considerable toxic hazard to humans [221]. Contact with the skin, the mucous membranes, and the conjunctiva leads to severe irritation and necrosis due to the hydrochloric acid formed by immediate hydrolysis. Contact with the eyes can cause blindness. The vapor leads to lachrymation and to irritation of the lower respiratory tract, with the danger of lung edema. In animal experiments the development of lung edema was more rapid and the death rate after exposure to TiCl_4 was higher than with an equivalent concentration of HCl alone, since HCl adsorbed on the particles of hydrolyzed TiCl_4 is transported to deeper parts of the respiratory tract which usually are not reached by the highly water soluble HCl [222].

Chronic Toxicity. In a long-term study of up to 390 d with various species, but very low numbers of test animals (two guinea pigs, two rabbits, four cats, one dog), the animals received between 0.6 and 9 g technical grade TiO_2 per day. There were no adverse effects and no histological abnormalities in any of these animals [223]. In a long-term study with

mice from weaning to natural death, the addition of 5 mg of titanium potassium oxalate per liter of drinking water led to a decrease of the survival rate after 18 months, which was slight in female mice and more pronounced in male mice [224]. The titanium-fed mice generally showed a higher body weight.

Inhalation of TiO_2 dust by rats for a period of up to 13 months (4 times per day, 5 d per week), followed by a 7-month period of fresh air, did not lead to any pathological effect on the lungs; the weight of the rats remained unchanged [225]. In another inhalation study (10–250 mg/m³ for 6 h/d, 5 d/week) performed for 2 years with rats, exposed groups showed an increase in the incidence of pneumonia, tracheitis, and rhinitis with squamous metaplasia of the anterior nasal cavity. Rats exposed to 50 and 250 mg/m³ showed various signs of disturbance of respiratory tract function and dust deposition in the tracheobronchial lymph nodes [226] (see also "Genotoxicity"). These findings were confirmed in detail by an analogous study in which an accumulation of TiO_2 was observed in the upper respiratory tract, lungs, gastrointestinal tract, lymphatic system, liver, and spleen [227].

Similar results concerning effects on respiratory tract function were obtained in a long-term study with rats exposed to TiCl_4 (0–10 mg/m³, 6 h/d, 5 d/week) for two years [228].

Ti compounds such as the hydride, carbide, and boride as well as potassium octatitanate and titanium phosphate fibers apparently are fibrinogenic in animal tests [210].

In humans, the most pronounced effects of a chronic occupational TiO_2 exposure appear in the respiratory system [decreased FEV₁ (Forced Expiration Volume during the first second) and FVC (Forced Vital Capacity)], resulting from deposition of TiO_2 in the lung [229].

A case of TiO_2 pneumoconiosis accompanied by lung cancer and slight fibrosis of the interstitium around bronchioles and vessels has been observed with a fifty-three-year-old man who had been employed for about thirteen years with packing of TiO_2 [230].

Genotoxicity. In an inhalation study with TiO_2 dust (10–250 mg/m³ for 6 h/d, 5 d/week) performed for two years with rats, there was an increased incidence of bronchioalveolar adenomas and cystic keratinizing squamous cell carcinomas as well as excessive dust loading in the lung of the 250 mg/m³ exposure group [226, 227]. These tumors were different from common human lung cancers with respect to tumor type, anatomic location, and tumorigenesis, and were devoid of tumor metastasis [226]. In a ³²P postlabeling assay for the detection of DNA adducts, TiO_2 formed one of the two DNA adducts that could be quantitated separately [228]. In contrast, up to 5% TiO_2 in the diet during 130 weeks did not cause carcinogenic effects in rats [231].

According to the IARC [232], there is inadequate evidence for the carcinogenicity of TiO_2 in humans, and limited evidence for the carcinogenicity of TiO_2 in experimental animals. TiO_2 is not classifiable as to its carcinogenicity to humans (Group 3).

Intratracheal administration of TiO_2 combined with benzo[a]pyrene to hamsters causes an increase in the incidence of benign and malignant tumors of the larynx, trachea, and lungs over that in benzo[a]pyrene-treated controls.

A two-year inhalation study with rats exposed to TiCl_4 (0–10 mg/m³, 6 h/d, 5 d/week) revealed an increased incidence of cystic keratinizing squamous cell carcinomas in high-dose groups [233].

The inhalation of fibrous potassium octatitanate by rats, hamsters, and guinea pigs has basically the same effects on the lungs as asbestos, although the effects are considerably less pronounced [234]. These findings were confirmed by an in-vivo test system [235].

Synthetic titanium phosphate mineral fiber shows a fibrinogenic potential in rats and hamsters after intratracheal injection, similar to that of asbestos; however, in contrast to the results with asbestos, no abnormal increase of the abdominal tumor rate after intraperitoneal injection of 2–10 mg/kg was observed [236].

Reproductive Toxicity. In a three-generation study with rats, the addition of titanium potassium oxalate to the drinking water (5 mg/L) led to a marked decrease in the number of animals surviving to the third generation [210]. In pregnant mice, the application of 30 or 60 mg/kg of the antitumor agent titanocene dichloride on day 10 and 12 resulted in the appearance of cleft palate in numerous fetuses and of costal malformations in some fetuses [237].

Immunotoxicity. In a group of dermatitis patients, no evidence of a skin sensitizing potential of TiO_2 could be observed [238].

Toxicological Data. Titanium dioxide, TiO_2 : TDLo (rat, intramuscular) 360 mg/kg [239]; titanium tetrachloride, TiCl_4 : LDLo (mouse, 2 h, inhalation) 10 mg/m³ [240]; LC₅₀ (rat, 4 h, inhalation) 460 mg/m³ [241]; calcium titanate, CaTiO_3 : LD₅₀ (rat, i.p.) 5300 mg/kg; barium titanate, BaTiO_3 : LD₅₀ (rat, i.p.) 3000 mg/kg; lead titanate, PbTiO_3 : LD₅₀ (rat, i.p.) 2000 mg/kg [210]; tetrabutyl titanate: LD₅₀ (mouse, i.v.) 180 mg/kg [242]; dicyclopentadienyltitanium: LDLo (rat, intramuscular) 50 mg/kg, LDLo (hamster, intramuscular) 83 mg/kg [239].

Treatment. After contact of the skin with TiCl_4 immediate dry removal (without use of water) is necessary. Thereafter, remaining traces of TiCl_4 should be removed with soap and plenty of water. After contact of the eyes with TiCl_4 , adequate measures are rinsing with plenty of water, use of Isogutt eye drops, and contacting an ophthalmologist as soon as possible. In cases of TiCl_4 vapor inhalation, cortisone preparations should be applied immediately (e.g., inhalation of Auxiloson) to avoid the development of lung edema. In severe cases clinical observation for at least 24 h is necessary.

Occupational Health. The MAK value is 6 mg TiO_2/m^3 , measured as total fine dust [243]. In the United States the ACGIH set a TLV value of 10–20 mg TiO_2/m^3 in 1980 [244].

Lung fibrosis caused by titanium and some of its compounds (carbide, hydride) is in-

cluded in the list of the German Berufs-krankheitenverordnung (Occupational Disease Regulations) [245].

Since TiO_2 tends to accumulate, persons heavily exposed at the workplace should undergo periodical medical examinations, including chest X rays and ventilatory function tests.

22.15 References

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